SYNTHESIS OF LOW BAND GAP POLYMERS

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Synthesis of Low Band Gap Polymers

by

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Abstract

A novel synthetic pathway to 4*H*-cyclopenta[2,1-*b*:3',4'-*b* ']dithiophen-4-one **2-8**, which is a valuable precursor for a variety of low band gap polymers, has been developed. From **2-8**, the derivatives 4,4'-bi-(4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophenylidene) **2-34** and 2,6-dibromo-4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophen-4-one **2-36**, were prepared. A poly(4*H*-cyclopenta[2,1-*b*:3',4'-*b* ']dithiophen-4-one) (poly **2-8**) film was modified by chemical reaction with Lawesson's reagent giving a new material, which exhibited a smaller band gap (0.8-1.0 eV) than the starting poly **2-8** (1.1-1.2 eV). Compound **2-34** was electrochemically polymerized and cyclic voltammetry showed that the resulting polymer has a low band gap (0.5-0.9 eV), consistent with a theoretical prediction. Compound **2-36** is a useful starting material for the synthesis of new polymers.

The known compound 2,2'-(ethyne-1,2-diyl)bis(thiophene) **3-3** was synthesized using an adaption of a literature procedure, and **3-3** was used for the synthesis of its novel derivatives 4,5-di-thiophen-2-yl-1,3-dithiol-2-one **3-5** and tetrathien-2-yl-thiophene **3-6**. Electrochemical polymerization of **3-6** gave a polymer with a band gap of *ca.* 1.8 eV.

Dithieno[3,2-*c*:2',3'-*e*][1,2] dithiin **4-1** was prepared by using a literature method. Electrochemically prepared films of poly **4-1** did not show any electroactivity for the disulfide bridge in acetonitrile.

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Contents

Glossary of Abbreviations

bp	boiling point
CV	cyclic voltammogram
DMF	*N,N*-dimethyl formamide
E	potential
E_g	band-gap
HOMO	highest occupied molecular orbital
ITO	indium tin oxide coated glass electrode
LUMO	lowest unoccupied molecular orbital
mp	melting point
MS	mass spectrometry
NBS	*N*-bromosuccinimide
NIR	near infrared
NMR	nuclear magnetic resonance (spectroscopy)
SSCE	saturated solution potassium chloride calomel electrode
THF	tetrahydrofuran
p-TsOH	*para*-toluenesulfonic acid
UV	ultraviolet
Vis	visible

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Chapter 1

Introduction

1.1 History:

The insulating properties of most polymers represent a significant advantage for many practical applications of plastics. During the last 20 years, however, organic polymers characterized by good electrical conductivity have been found. Due to their low density, good processibility, and resistance to corrosion, and the exciting prospects for plastics fabricated into electrical wires, films, or electronic devices, these materials have attracted the interest of both industrial and academic researchers in domains ranging from chemistry to solid state physics to electrochemistry. The close interaction between scientists from diverse backgrounds has been a significant factor in the rapid development of the field of conducting polymers [1-3].

A key discovery was made in 1973, when the inorganic polymer polysulfurnitride $(SN)_x$ was found to exhibit a metallic conductivity [4]. The conductivity of $(SN)_x$ at room temperature is about 10^3 $S.cm^{-1}$; below a critical temperature of about 0.3 K, $(SN)_x$ becomes a superconductor [5]. Unfortunately, $(SN)_x$ is explosive and no commercial applications were possible.

At the end of the 1970s, Chiang *et al.* [6] discovered that polyacetylene $(CH)_x$, synthesized following the method of Shirakawa and coworkers [7], could become highly conducting on exposure to oxidizing or reducing agents. This finding can be considered the starting point of the modern era of conducting polymers. It is worth noting that polyacetylene had been synthesized in 1958 by Natta *et al.* [8] with the intention of obtaining a conducting polymer. As a matter of fact, when polyacetylene is doped, it becomes highly conducting (up to 10^6 $S.cm^{-1}$) [9, 10].

The process of oxidation or reduction of a neutral polymer is often referred to as "doping" by analogy to inorganic semiconductors. However, this analogy is certainly not accurate, and the

processes must be viewed as redox reactions. The original neutral polymer is converted into a salt consisting of a polycation (or polyanion) and counterions, which are the reduced forms of the oxidizing agent (or the oxidized forms of the reducing agent). If solid-state physics language is used, oxidation corresponds to *p*-type doping and reduction to *n*-type doping.

An extended polyconjugated structure is fundamental for organic conduction. Even if practical applications of $(CH)_x$ are limited by its environmental instability, polyacetylene is the simplest example of this class of material and is still the object of intensive theoretical and experimental research [11].

Polyheterocycles constitute another class of conducting polymer. They can be regarded as a conjugated carbon chain with the (*s-cis*)-*trans*-polyacetylene conformation of the polyacetylene backbone enforced by the heteroatom (Figure 1-1). These conducting polymers differ from polyacetylene in many ways. Their ground state is non-degenerate because of the lack of energetic equivalence of their two limiting mesomeric forms, aromatic and quinoid [12], limiting mesomeric forms are energetically non-equivalent and they are generally more stable. Moreover, their structure may be readily modified by substitution, allowing the modulation of their chemical, electronic, and electrochemical properties.

In 1979, it was reported [13] that polypyrrole could be obtained as a freestanding film by electrochemical oxidation of pyrrole in acetonitrile. The polymer was produced at the electrode surface and could be peeled off as a flexible, relatively dense, shiny, blue-black film. Polypyrrole had already been synthesized electrochemically from aqueous sulfuric acid solutions in 1969 by Gardini and coworkers [14], but the poor mechanical and electrical properties of the material obtained discouraged further developments of this synthetic method. In 1982 Tourillon *et al.*

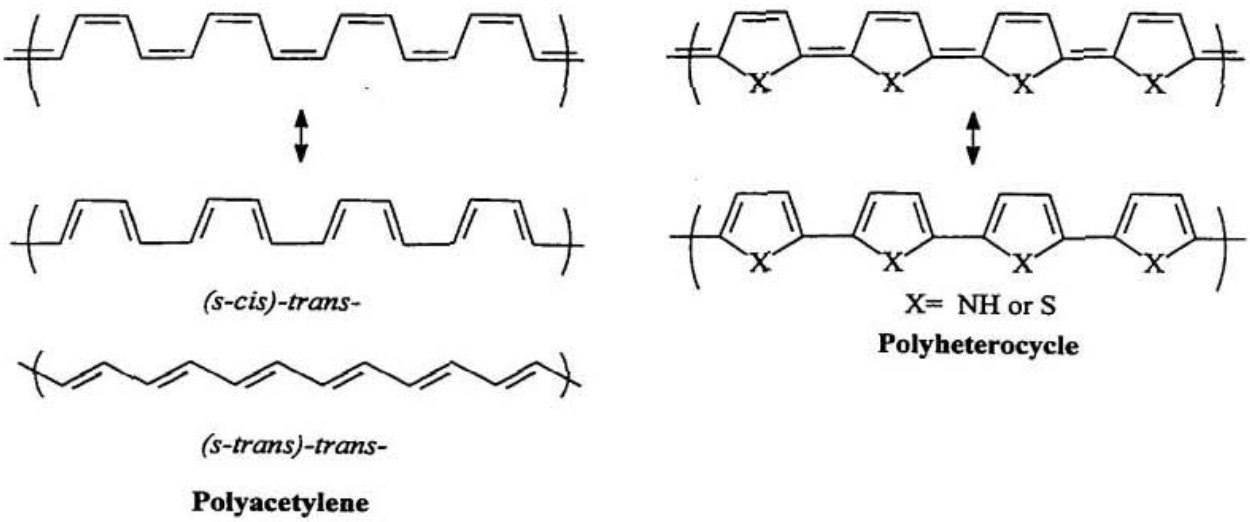


Figure 1-1. Polyacetylene in Comparison with Polyheterocycles.
[15] prepared polythiophene by the anodic oxidation of thiophene.

In the electrochemical method, the potential of polymerization can be controlled and the quality of the polymer optimized. Moreover, the polymers are obtained in the *p*-doped state as films suitable for further electrochemical study. Therefore, in this field, electrochemistry plays both synthetic and analytical roles. Quickly the electrochemical polymerization method was extended to other aromatic compounds such as furan, indole, carbazole, azulene, pyrene, benzene, and fluorene, and electrochemical synthesis is now the most widely used technique for the preparation of conducting polymers [15-17].

1.2 Band Gap

According to band theory, in the solid state, the atomic orbitals of each atom overlap with the orbitals of neighboring atoms in all directions to produce molecular orbitals. When these orbitals are grouped in a range of energies, they form continuous energy bands. The energy spacing between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is called the energy gap or band gap (E_g). In other words, E_g is the energy difference between the top of the valence and the bottom of the conduction band [18].

Band filling determines the electrical properties of conventional materials. In a semiconductor, E_g is relatively narrow and thermal excitation of electrons from the valence band to the conduction band gives rise to conductivity. If the band gap is too wide and electrons cannot be excited at room temperature across the gap, the material is an insulator. The high conductivity of metals comes from a partially occupied band or a zero band gap (Figure 1-2). A major goal in the work on conducting polymers is to minimize E_g, to maximize their intrinsic conductivity [1-3].

In order to design low band gap polymers, guidance comes from two main sources. On one hand, an understanding of what are the theoretical elements that contribute to the band gap, and on the other hand, explanations of the empirical behavior of specific polymers.

Taking the specific example of a polyheterocycle (Figure 1-3a), the total E_g can be decomposed into the basic terms given in the following equation [2]:

$$E_g = E^{\delta\pi} + E^{\theta} + E^{Res} + E^{Sub} + E^{int}$$

This equation makes clear the various structural variables that have to be mastered in order to control the gap of conjugated systems.

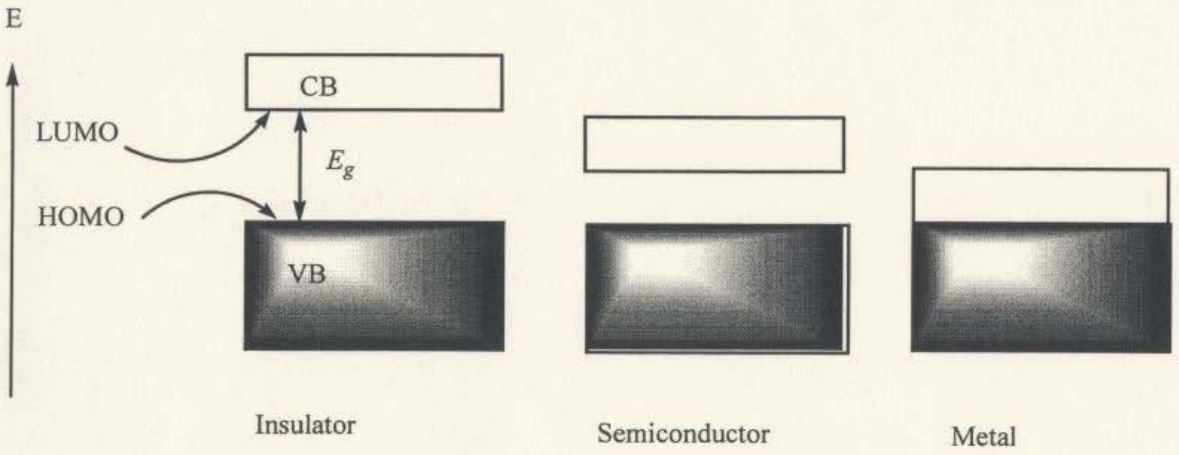


Figure 1-2. Illustration of Band Gap in Different Materials.

As outlined below, "bond length alternation" ($E^{\delta r}$) is one of the major factors contributing to the existence of a finite E_g. Orbital overlap varies approximately with the cosine of the torsion angle θ between monomer units [19, 20], and so any deviation from coplanarity will increase the contribution given by the term E^{θ}. The competition between π-electron confinement within the rings and delocalization along the chain (Figure 1-3b) is represented by E^{Res} [21]. The most widely studied way to reduce E_g is modification of the HOMO and LUMO levels by introducing electron donating or electron releasing substituents into a particular monomer (E^{Sub}) [22, 23]. Although intramolecular conductivity depends on the chain polymer length, it has a finite size, and the Peierls distortion decreases the importance of long range conjugation, therefore, good intermolecular conductivity, which is related to the interaction between polymer chains is considered in the term E^{int} [24].

1.3 Bond Length Alternation

Good mobility of electrons in a polymer requires an extended conjugated system. For any polyheterocycle, there will be two limiting resonance structures. The "aromatic structure," in which monomer units are linked to each other by single bonds (Figure 1-4 a), can adopt any twisted spacial arrangement, because the π-electrons are largely localized in the individual rings. As a consequence, there is little interaction between rings (Figure 1-4 b and 1-4 c). On the other hand, the "quinoid structure" (Figure 1-4 d and 1-4 e), where there are no aromatic rings, exhibits significant delocalization through the polymer backbone and should have a planar structure. In between, there are a large number of possible combinations, with the polymer having regions with "aromatic" and "quinoid" structures.

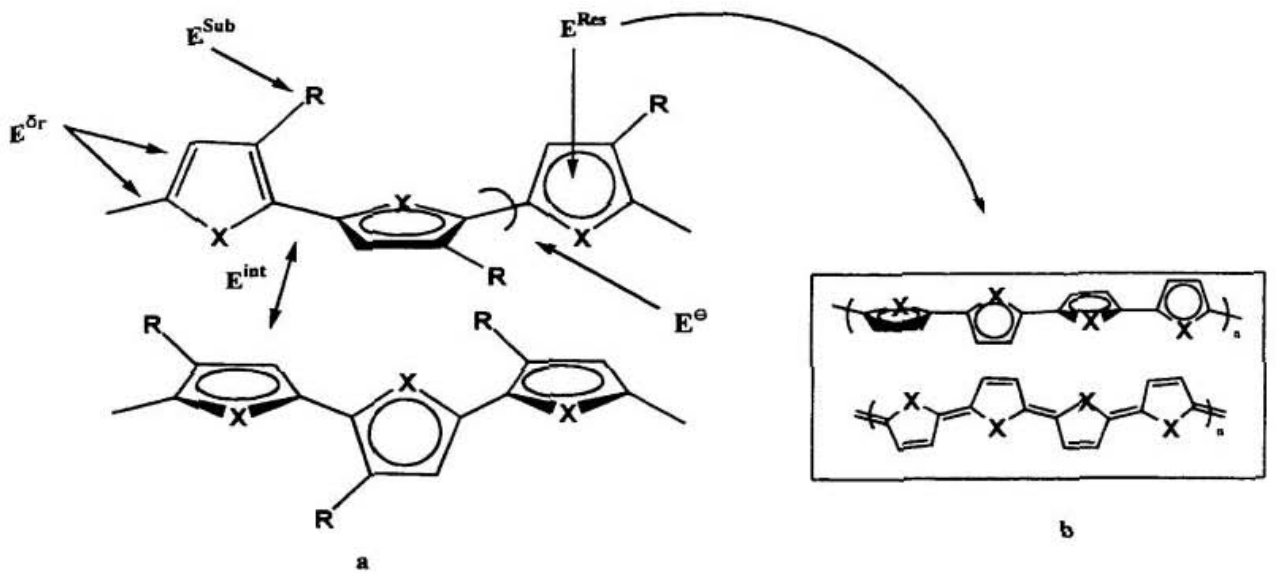


Figure 1-3. Contributions to Energy of the Band Gap.

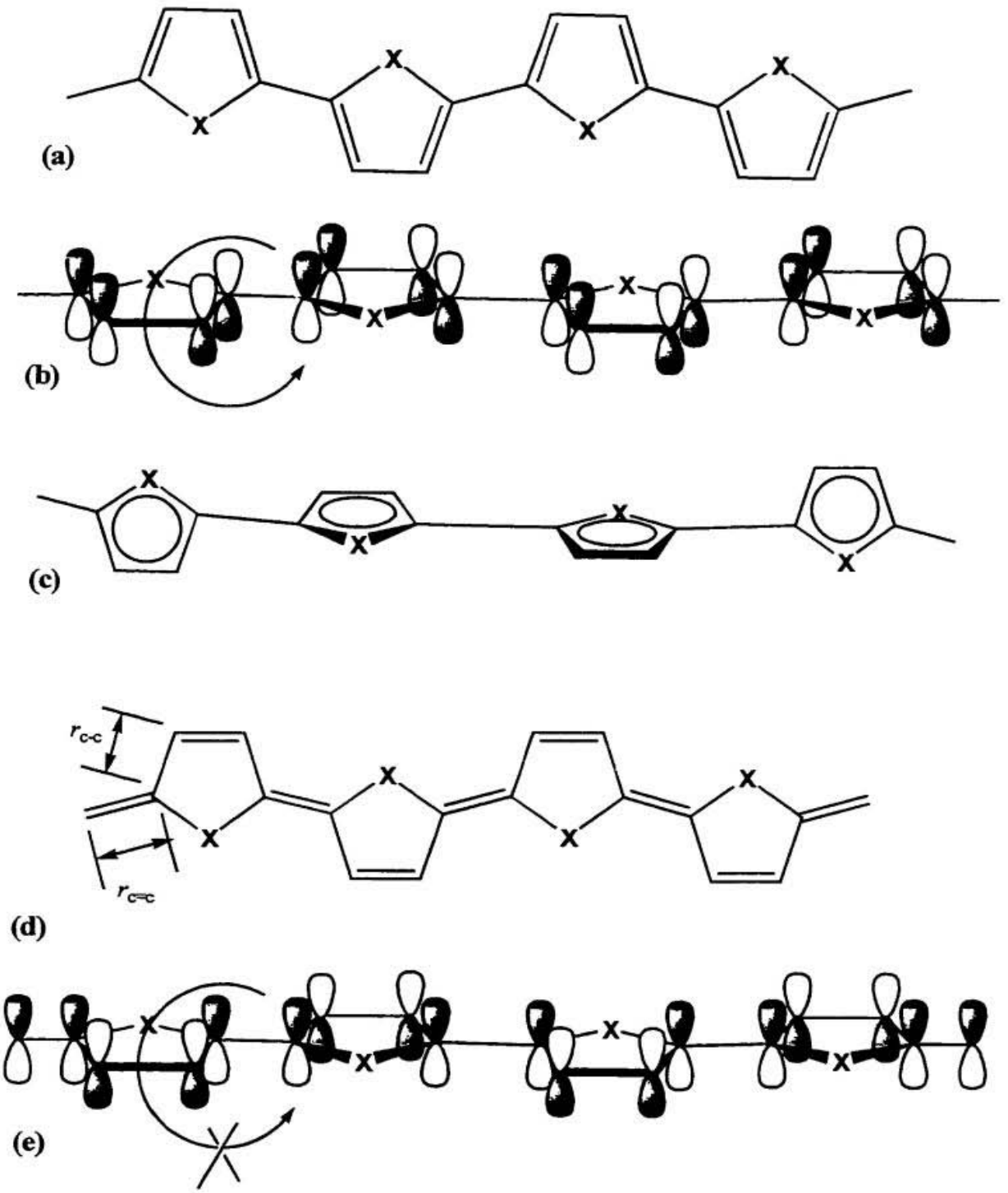


Figure 1-4. Structures and Bond Length Alternation in a Polyheterocycle.

As was described before, the most important contribution to E_g is due to "bond length alternation" ($E^{\delta r}$). This term is described as $E^{\delta r} = k\delta_r$ where $k \approx 15$ eV/Å and δ_r is the difference between the single and double bond ($r_{c\text{-}c} - r_{c=c}$) (Figure 1-4d) [25].

1.4 Synthesis of Conducting Polymers

1.4.1 General considerations

The choice of a synthetic method depends on the type of conducting polymer and the macroscopic form of the required material. Very often the material is needed as a thin film, either for characterization or as a sensor material, for example. Use of a bulk chemical method for the synthesis usually produces the polymer as an insoluble powder. If the polymer can be dissolved in some solvent, the fabrication of films may not be a problem, but often conducting polymers are completely insoluble, intractable, and infusible solids. Then, if applicable, electrochemical synthesis is an appropriate choice. In certain cases it is possible to synthesize a precursor polymer that is soluble, allowing a facile method for film fabrication and easy transformation to the final product.

The number of synthetic methods for producing conducting polymers are continually appearing. The trend has been to synthesize relatively low molar mass oligomers either as well-defined models for conducting polymers or for practical applications. Most of the new synthetic methods have been developed in this connection, but often they are also applicable to polymers.

1.4.2 Polymerization Methods

1.4.2.1 Chemical Polymerization

Usually the synthesis of conducting polymers requires the formation of carbon-carbon bonds. In the cases of pyrrole [13, 26-28] and thiophene [29, 30] the most common method is oxidative coupling. This can be done in two ways, either chemically or electrochemically, the mechanism being the same in both cases (Section 1.4.2.2.1).

The nature of the radical generated has a crucial influence on the process. If it is too reactive, reactions with solvent and impurities will compete with the polymerization reaction. On the other hand, if the radical is too stable, the following steps will be slow and the resulting polymer will have a low molar mass. Therefore, only radicals with optimal reactivity will produce a high molar mass polymer.

The solvent and the electrolyte play a very important role (Section 1.4.2.2.2). For example, increasing the nucleophilicity of the solvent may improve the quality of the resulting polymer. However, this is not general and depends on the particular monomer. The most common oxidants used for chemical polymerization are Fe(III), Cu(II), and peroxydisulfate ($S_2O_8^{2-}$) [31].

Other chemical polymerization methods are based on the use of organometallic reagents, and can roughly be divided into two sections, homocoupling and heterocoupling, depending on whether the monomers are identical or not.

The oldest homocoupling method known is the Ullman coupling [32, 33], which consists of the reaction between an iodoaromatic compound and copper(0). The organocopper

intermediate thus generated then reacts with another molecule of the iodoorganic compound. Poly(*p*-phenylene), for example, has been prepared using this method (Figure 1-5a). Copper compounds have also been used in the coupling of organolithium compounds, and some thiophene oligomers can be prepared in this way [34].

Grignard compounds have been coupled with organohalogens by using nickel complexes as catalysts. For example Kobayashi *et al.* [35] have reported the preparation of polythiophene from 2,5-diiodothiophene. They also prepared polythiophene starting from 2,5-dibromothiophene. Organozinc compounds can be used in the same way (Figure 1-5b) [34].

Organotin [36] and organoboron [37] compounds have become rather common in preparing oligomers, as has the use of palladium complexes as catalysts. An advantage of these approaches is that the reagents have a high tolerance to other substituents in the molecule, in contrast to the organomagnesium and organozinc reagents (Figure 1-5c).

Palladium induced coupling with organotin compounds is widely called Stille coupling [38] (Figure 1-5d), and has also been utilized as a heterocoupling method. The reaction must be carried out in a dry solvent under a nitrogen atmosphere.

Palladium induced organoboron coupling is known as Suzuki coupling [37, 39] (Figure 1-5e), and is less sensitive to water. In fact, it is often carried out in water or aqueous solutions. Nevertheless, oxygen must be avoided.

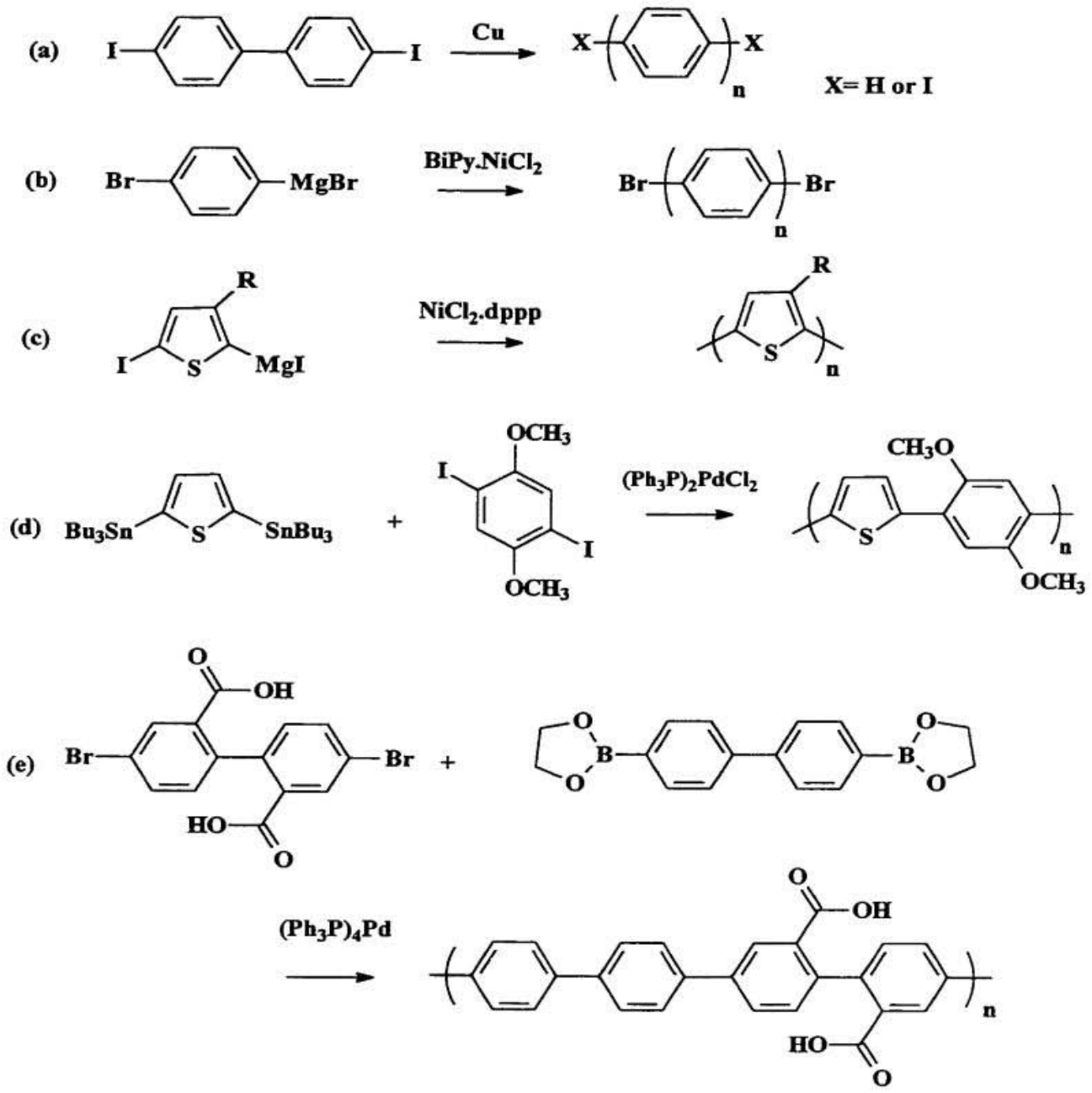


Figure 1-5. Examples of Synthetic Reactions for Producing Conducting Polymers.

1.4.2.2 Electropolymerization

Electrochemical polymerization has played a critical role in the development of conductive polymers [15, 29], with oxidative electropolymerization being widely used, whereas reductive polymerization is rarely applied.

In electropolymerization, three electrodes are mounted in an electrolysis vessel, which contains an electrolyte solution and the monomer. As current flows the polymer is deposited on the anode. Then either the anode with its polymer layer is used for characterization procedures, or the layer may be peeled off from the anode surface and used as a film. The success of the latter depends of the physical characteristics of the polymer.

The oxidized form of the polymer, produced by electropolymerization, will contain positive charge carriers, which may be in the form of *polarons* or *bipolarons*. These charges must be compensated for by a corresponding negative charge. Thus anions from the electrolyte are incorporated into the growing film during the polymerization process. It is logical, therefore, to conclude that the size and character of the anions will be important in determining the quality and the properties of the polymer (Section 1.4.2.2.2).

1.4.2.2.1 Mechanism of Electropolymerization

The mechanism can be divided into several steps [40] (Figure 1-6). The first step is the oxidation of the monomer to a radical-cation. The unpaired electron and positive charge are delocalized in the ring, and quantum mechanical calculations show that the spin density is highest at the 2 and 5 positions. Consequently the reactivity for coupling is highest at these

positions [43].

In the second step the radicals form a dimer, and subsequent deprotonation is energetically favorable because the two extra protons disturb the aromaticity. Once formed, the dimer is easily oxidized. As a matter of fact, because of the larger conjugated system it is even more easily oxidized than the monomer. The oxidized dimer then reacts with another monomer radical and so on.

Coupling of two radicals occurs most readily between the locations of highest spin density. According to quantum chemical calculations, the highest spin densities are at the terminal α-positions [43]. However, the larger the conjugated system, the wider the region over which the electron density is distributed, and so with the growing conjugated system there is an increasing tendency for radicals to react at other locations besides α. This results in discontinuities in conjugation, branching and cross-linking.

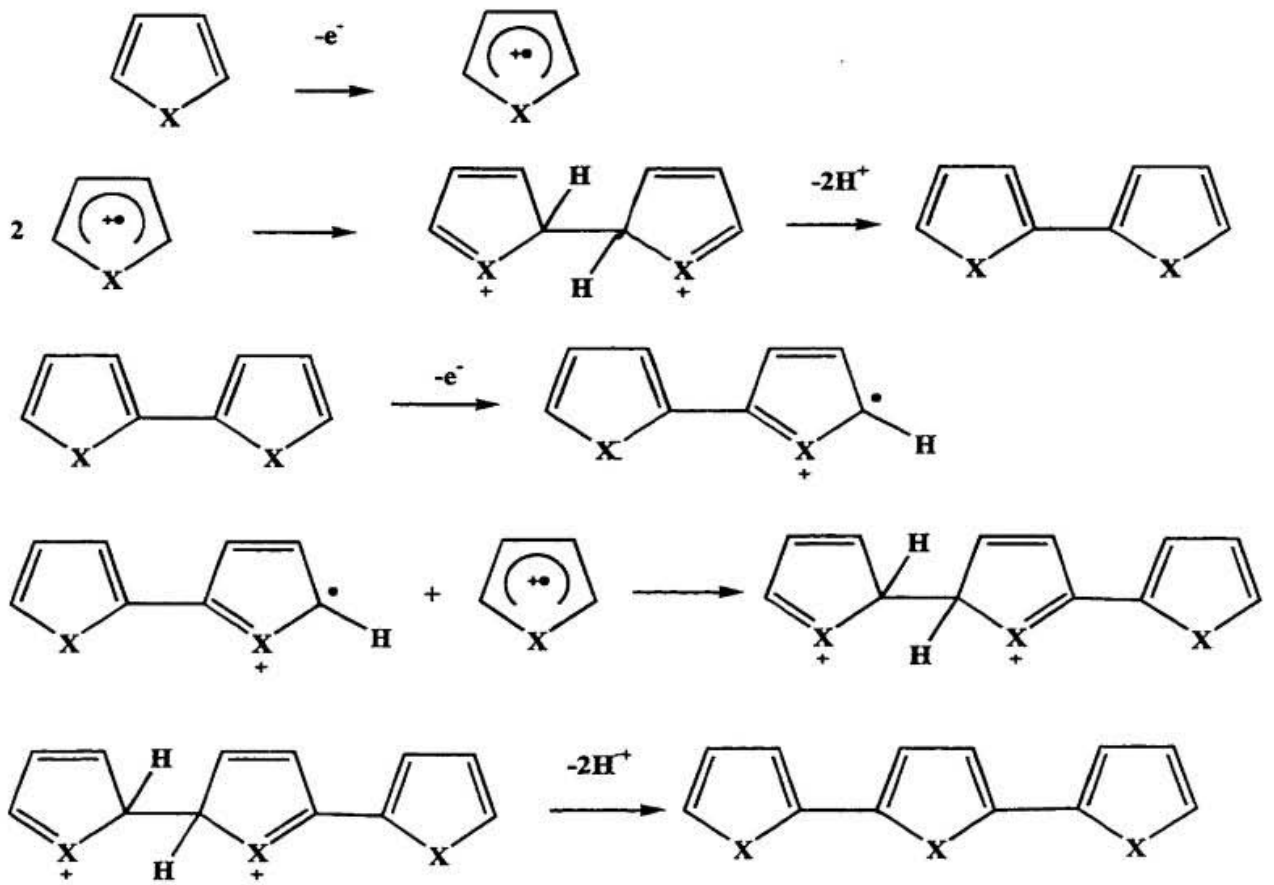


Figure 1-6. Oxidative Polymerization Mechanism.

1.4.2.2.2 Effects of Electrosynthesis Conditions

The structure and properties of a polymer generated by electropolymerization are strongly influenced by the experimental conditions, such as the solvent, reagent concentration, cell geometry, nature and shape of the electrodes, and all the applied electrical conditions.

The dielectric constant of the solvent must be sufficiently high to ensure the dissolution and dissociation of the supporting electrolyte and, consequently, the ionic conductivity of the electrolytic medium. The solvent must also show a potential window open at the potential required to oxidize the monomer.

Pyrrole can be polymerized in water [41]. However, this is an exception, and organic solvents are usually employed. Acetonitrile, nitrobenzene and benzonitrile [15, 29, 42-47] are the preferred solvents because of their high dielectric constants ($\epsilon = 37$ for acetonitrile, $\epsilon = 35$ for nitrobenzene, and $\epsilon = 25$ for benzonitrile) and their stability over a wide potential range (from 2.7 to -3.2 V vs. SSCE on platinum). Amides (dimethyl formamide: 1.5 to -2.5 V and $\epsilon = 37$), ethers (tetrahydrofuran: 2.1 to -3.3 V and $\epsilon = 7$), propylene carbonate (1.7 to -1.9 V and $\epsilon = 64$), and dichloromethane (1.8 to -1.7 V, $\epsilon = 9$) are also frequently used.

The presence of water affects the electropolymerization process. In the case of thiophene, trace amounts of water in the chosen organic solvent play a beneficial role, for reasons that have not yet been clarified. On the other hand, a significant amount of water in the solvent is detrimental, causing incorporation of carbonyl groups and adversely affecting the conjugation length and conductivity [48].

The favorable effect of water in the case of pyrrole is attributed to its proton scavenging action, which prevents protonation of pyrrole and the consequent increase in oxidation potential [49].

High monomer concentrations, such as 0.1 M or more, are generally used to minimize competing reactions of the radical cations or reactions of the oxidized polymer with nucleophiles present in the medium. However, the choice of monomer concentration depends mostly on the

oxidation potential of the monomer. If the monomer is oxidized at a low potential, the competition of side reactions decreases and even millimolar concentrations may be successfully used, as in the particular case of bithiophenes.

Regardless of whether the process is oxidative or reductive electropolymerization, counterions are incorporated into the material to balance the charges produced during the polymerization, and their influence is clearly important.

Once the polymer is formed, counterions affect its properties in different ways. The size and shape of ions affect their diffusion rates inside the polymer material. Incorporation of ions into compact and hydrophobic films is more difficult than into porous, hydrophilic films. Therefore, large anions do not appreciably diffuse into polythiophene films and these films can be doped only with small non-nucleophilic spherical anions, such as perchlorate (ClO_4^-) [15, 45-47, 50, 51], hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-) [52, 53], and trifluoromethane-sulfonate ($CF_3SO_4^-$) ions [54]. On the other hand, polypyrrole forms a more porous structure and is able to accept a wide range of counterions.

The mobility of very large counterions in the polymeric material is almost zero. The only way to introduce such ions into the polymer is during its preparation. These anions become immobilized in the polymeric material, neutralizing the positive charges on the oxidized polymer. During subsequent reduction, the positive charges disappear, and the negative charges of the immobilized anions must be neutralized by cations from the solution. In the resulting material the cations are the ionic charge carriers and their size and solvation are important factors in determining their mobility and the electrochemical behavior of the polymer. Polypyrrole doped with dodecyl sulfate ($CH_3(CH_2)_{10}CH_2SO_4^-$) [41, 55, 56] is a well-studied example of this

type of material.

The chemical structure of the counterion may also have a crucial influence on the morphology and conductivity of the polymer. For example, polypyrrole-dodecyl sulfate is very smooth, dense, stable, and highly conducting, whereas polypyrrole-perchlorate has an open and porous macro structure and a conductivity that is about 100 times lower [56, 57].

1.4.2.2.3 Modes of Electropolymerization

Electropolymerization can be done by potentiostatic (constant potential), galvanostatic (constant current) or potentiodynamic (continuously varying potential) methods [55, 58]. The potential (or current) is selected to ensure that undesirable side-reactions do not take place but the polymerization proceeds at a reasonable rate.

The galvanostatic method allows the thickness of the film to be easily regulated by controlling the polymerization time. However, the increasing film resistance may cause the potential to rise to a high level, causing side-reactions or degrading the film.

When the potentiodynamic method is chosen, the film experiences different potentials throughout the process and usually more stable and homogeneous films are usually formed.

1.4.3 Characterization Methods

The characterization methods used for conventional polymers are also useful for conducting polymers. For identification purposes different spectroscopic methods such as infrared spectroscopy [59, 60] and NMR [61, 62] are used. If the polymer is soluble, gel

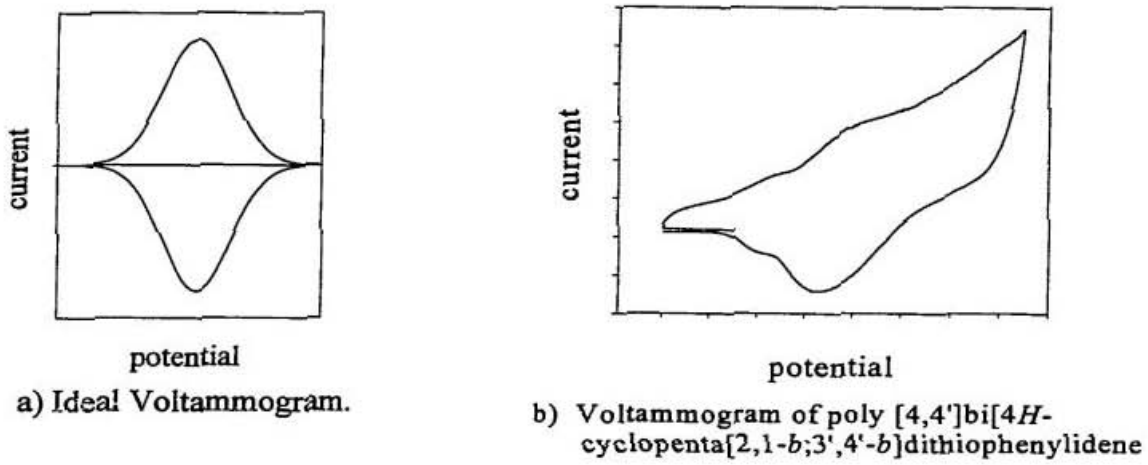
filtration methods may be used for the determination of molar mass. However, due to the electrical and optical properties of these kinds of polymer, and the intractability of many conjugated polyheterocyclic structures, other novel techniques can also, or must be used. Their electrical conductivity allows one to perform cyclic voltammetry (CV) on these materials, and, because of their conjugated nature, their absorption spectra extend into the visible or near infrared region.

1.4.3.1 Cyclic Voltammetry (CV)

Once again electrochemistry plays a particularly important role. Cyclic voltammetry [63] is normally one of the first methods to be applied to a new conducting polymer. As in traditional CV, a triangular shaped potential wave form is applied to the cell [64], but here the working electrode is coated with the polymer to be analyzed. The cell is filled with an electrolyte solution that usually does not contain any electroactive solute. When current flows, there is an electron transfer across the polymer electrode interface and ion transfer across the polymer/solution interface. If the polymer film is relatively thin, the diffusion time of ions is short and it is expected that the reverse electron transfer occurs exactly at the same potential on the return sweep of the CV. Therefore, voltammograms with symmetrical and mirror image cathodic and anodic waves should be expected [65-67].

An important point is that the current is directly proportional to the scan rate, whereas in conventional CV, where the transport of ions is limited by diffusion, the current is proportional to the square root of the scan rate. The idealized voltammogram (Figure 1-7a) is based on the

assumptions that the film is thin, (i.e., it approximates monolayer behavior) and the electrode process is fully reversible. As often happen in practice, these assumptions are not valid, and distortions of the symmetry of the voltammogram appears. When the charge transfer rate is slow, the two waves shift away from each other and the voltammogram becomes asymmetrical. If the film is thick, there will be a slow migration of charge compensating ions, and this causes a square root dependence of the peak current on the scan rate (Figure 1-7b).



a) Ideal Voltammogram.

b) Voltammogram of poly [4,4']bi[4*H*-cyclopenta[2,1-*b*;3',4'-*b*]dithiophenylidene

Figure 1-7. Ideal and Actual Cyclic Voltammograms.

Other important factors to be taken into account are that the electropolymerized film will consist of different chain length polymers, and as a result will have different redox potentials, which causes the broad shape of the cyclic voltammograms. Also, the character of the material is quite different in the undoped and doped state. In the undoped state the polymer is generally

non-polar and often hydrophobic, while in the oxidized, doped form it will be more polar and even hydrophilic, so it can be predicted that the redox current will behave differently depending on the direction in which the potential is scanned.

One of the values of CV is that it allows the determination of the band gap (E_g) of the material. When the polymer under investigation can be both *p*-doped (oxidized) and *n*-doped (reduced), E_g is given by the difference between the onset of the oxidation wave and the onset of the reduction wave (Figure 1-8).

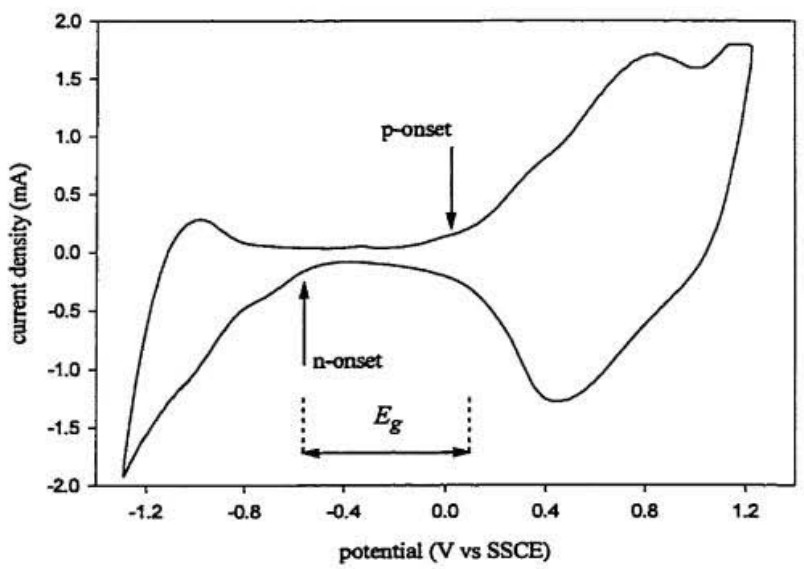


Figure 1-8. Band Gap from Cyclic Voltammogram.

1.4.3.2 Spectroelectrochemical Methods

Conducting polymers are polyconjugated molecules, with the consequence that the electronic energy levels are close enough to provide transitions in the visible and near infrared regions. There are three different method groups for measuring the absorption spectrum of a thin polymer layer, which are based on reflection, transmission and photoinduced charge transfer. The most widely used methods are based on transmission.

The basic requirement is to utilize an electrode material, that is transparent in the spectral region to be used for the characterization of the polymer film. Currently, indium-tin oxide-coated glass (ITO) is the most extensively employed. It is transparent down to 350 nm and into the near infrared. Its surface resistivity varies depending on the source and intended application but is usually between 10 and 300 Ω cm^{-2} [68, 69].

1.5 Low Band Gap Polymers

The synthesis of polymers with low energy gaps (E_g), better known as *Low Band Gap* polymers, is a goal of considerable current research due to the possible elimination of doping [70]. A wide range of low band gap polymers has already been reported. These polymers can be classified into different groups, according to the chemical nature of the precursor monomer [2]. Selected examples will be presented to illustrate the variety of strategies that have been employed.

In early theoretical studies by Brédas *et al.* [71], the band gap of polyheterocycles was reported to depend markedly on the molecular geometry. For example, polythiophene had been

reported to have a band gap of about 2 eV, which agreed with the calculated value for the aromatic geometry, but is far from the calculated value for the quinoid geometry (0.47 eV). Experimental confirmation of these studies has been reported by Kobayashi *et al.* [72] in their work with polyisothianaphthene **1-1** (Figure 1-9). The experimental E_g of 1.13 eV is consistent with the preferred stabilization of the quinoid conformation **1-1b** (instead of **1-1a)** induced by the fused benzene ring.

Along the same research line, dithieno[3,2-*b*:2',3'-*d*]thiophene **1-2** [73], has been polymerized electrochemically. This polymer has a low energy gap (E_g = 1.1 eV) [74], good conductivity and stability.

An originally empirical method to reduce the band gap of a polymer is the use of a comonomer which already contains α,α' linkages, to produce a copolymer containing less α,β' conjugation defects. Examples of these kinds of monomers are **1-3** (E_g polymer = 1.70 eV) [75], **1-4** (E_g polymer = 1.40 eV) [76], and **1-5** (E_g polymer = 0.50 eV) [77].

Based on the idea that alternation in the polymer chain of strong donor and acceptor units would draw the HOMO and LUMO levels closer together, Huang and Pickup [78] reported the synthesis of copolymers from mixtures of **1-7a** and **1-7b** (E_g polymer of 0.33 to 0.16 eV or even close to zero, depending of the amount of 3,4-ethylenedioxythiophene **1-7a** incorporated into the copolymer). Following with the idea, Havinga *et al.* [79] also reported the preparation of the polymer **1-6** (E_g = 1.2 eV).

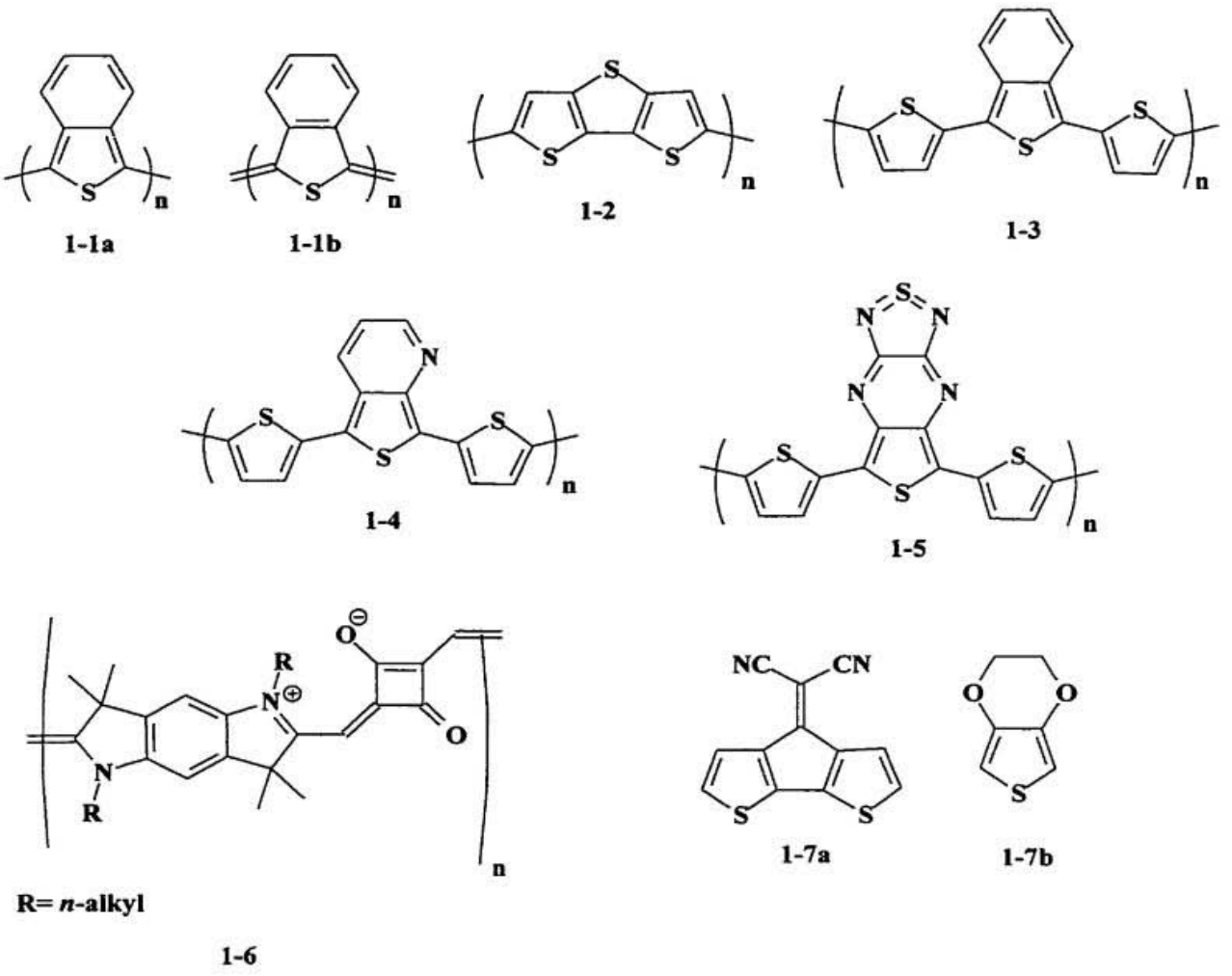


Figure 1-9. Examples of Precursors for Low Band Gap Polymers

1.5.1 Bithienyls

Since the pioneering work by Ferraris and Lambert [80, 81], who reported the electropolymerization of cyclopenta[2,1-*b*:3',4'-*b* ']dithiophen-4-one **2-8** (Figure 1-10) (E_g

polymer = 1.1-1.2 eV), a group of 2,2'-bithiophenes bridged at the 3,3'-positions with different substituents have been extensively studied not only experimentally [3,80-86], but also theoretically [87-90]. The approach is based on the concept that the electron-withdrawing effect of the introduced carbonyl group at the sp^2 hybridized bridging carbon decreases the aromaticity of the system, therefore, increasing the quinoid character of the polymer.

Similarly, 4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b*']dithiophene **1-8** was found to have a low E_g (E_g polymer = 0.80 eV) [81], and Huang and Pickup [91] have reported conductivity studies of this polymer. Another example is cyclopenta[2,1-*b*;4,3-*b*']dithiophenylidene-4-[cyano(nonafluorobutylsulfonyl)]methane **1-9** (E_g polymer = 0.67 eV) [92].

Introduction of an electron donating group, such as a 1,3-dithiole moiety, at the sp^2 bridging carbon provides the precursor **1-10**, which also gives a low band gap polymer (E_g polymer < 1.4 eV) [93]. Compounds **1-11** (E_g polymer = 1.40 eV) [108] and **1-12** (E_g polymer = 0.9 eV) [84] have also been reported.

The reduced band gaps of the polymers derived from precursors **1-11** and **1-12**, which are bridged by an sp^3 hybridized carbon atom, and compound **1-10** requires a different explanation than that given for compounds **2-8, 1-8** and **1-9.** Although coplanarity and a decreasing bond length alternation surely play an important role, the theoretical explanation is still being debated [94, 95].

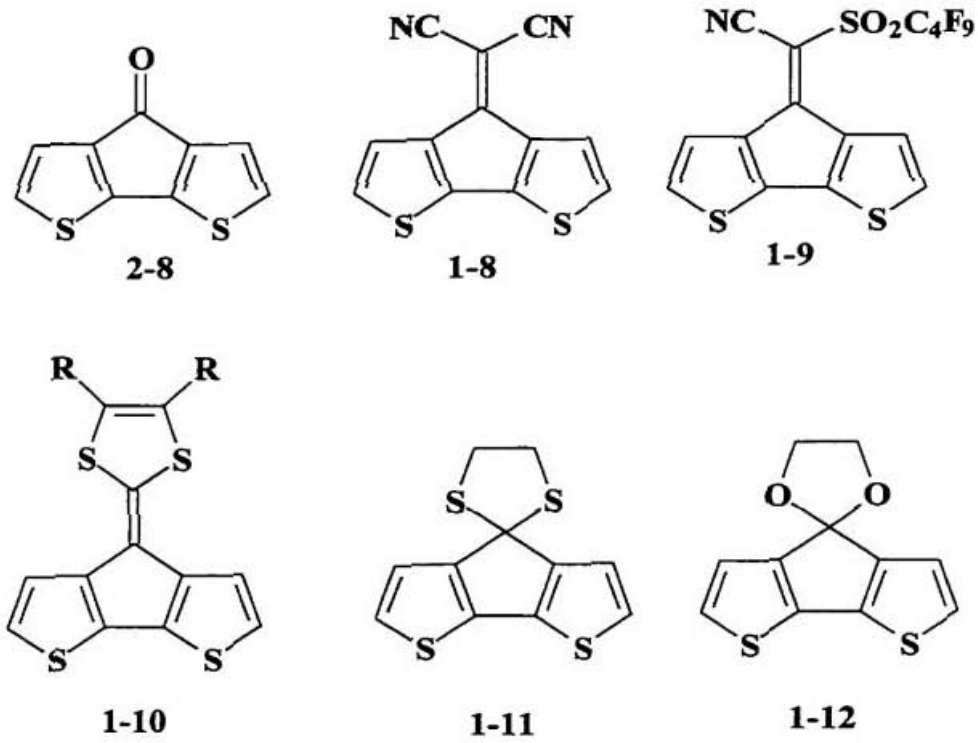
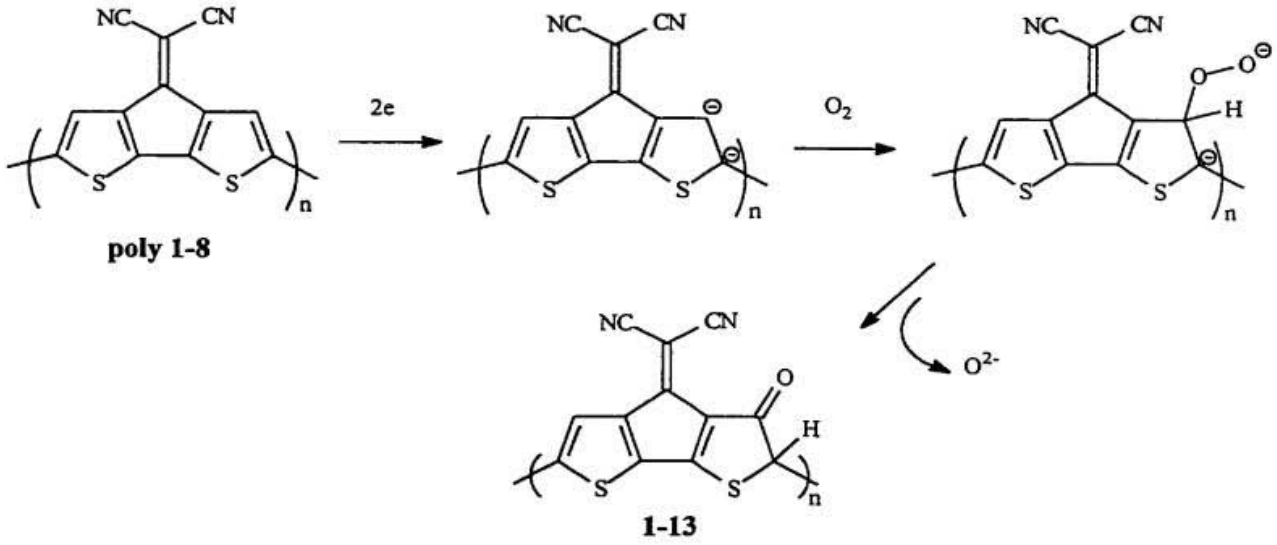


Figure 1-10. Examples of Bithienyls Precursors for Low Band Gap Polymers.

Recently, it was reported [96] that the reaction of n-doped poly(4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*; 3,4-*b*']dithiophene) (poly **1-8**) with O_2 at negative potentials produces a modified polymer **1-13** with a lower band gap (as low as 0.19 eV) (Scheme 1-1).



Scheme 1-1. Proposed Substitution Reaction for Poly(4-dicyanomethylene-4*H*-cyclopenta [2,1-*b*;3,4-*b*']dithiophene).

1.5.2 Polymers Based on the Spacer Strategy

Another method for modifying the redox potential of pyrrole and thiophene based polymers is by the "spacer strategy" [97]. According to this idea, the starting monomers consist of two external pyrrole or thiophene rings linked through a conjugated spacer. The spacer should be designed to meet the following requirements: (1) it should behave as a substituent on the attached heterocycle, in order to modulate the electronic characteristics of the heterocycle, which would affect the redox potential E^0 of the final polymer, and (2) it should represent an element of further functionalization with suitable groups in order to give the final polymer specific properties, thus controlling solubility, brittleness, etc.

1.6 Aims of this work

It can be easily inferred that ketone **2-8** occupies a special position in this field since many bithiophene precursors of small band gap polymers reported so far are derivatives of this molecule. The first goal of this work, which is described in Chapter 2, was the synthesis of new derivatives of the compound **2-8** that would be potential precursors for low band gap polymers. However, because of the length of the literature pathway to **2-8** [99] and the low yield of an intermediate step, improvement of the synthesis of **2-8** became an intermediate goal.

Chapter 3 describes the synthesis and functionalization of the known compound **3-3**, which has been utilized by Zotti *et al.* [118] as a precursor to conducting polymers based on the "spacer strategy." The reactivity of the triple bond allows facile functionalization of the linkage between the two thiophene rings (compounds **3-5** and **3-6**). This functionality was targeted because of its anticipated lowering of the band gap.

The synthesis of compound **4-1** is described in Chapter 4. Compound **4-1** was considered to be a potential precursor for low band gap polymers, as well as a useful material for charge storage in the cathode of a lithium (or lithium ion) battery [131].

The electropolymerization of the new compounds, cyclic voltrammetric analysis, as well as characterization by UV-VIS spectroscopy are developed in Chapter 5, providing confirmation of low band gaps in some of the new materials developed.

Chapter 2

Synthesis

of

4*H*-Cyclopenta[2,1-*b*:3',4'-*b*']dithiophen-4-one

Derivatives

2.1 Introduction

This chapter is concerned with the synthesis of 4*H*-cyclopenta[2,1-*b*:3',4'-*b'*]dithiophen-4-one **2-8** (Figure 2-1), and its derivatives. Despite the importance of compound **2-8**, which can be inferred from the amount of work published in recent years on it and its derivatives [2, 3, 80, 82, 84, 86, 87, 97], there have been few improvements in its synthesis. The primary idea at the beginning of this work was to simplify the synthetic route as a prelude to the synthesis of some new derivatives. Analysis of the related literature revealed the possibility of a completely different strategy to achieve the molecule **2-8**.

The original synthetic strategy (Section 2.2.1) was based on the formation of the central ring from the acyclic ketone **2-5**. It required protection of the ketone, and then activation of the 2 positions of the thiophene units for a subsequent Ullmann ring closure (Route I, Figure 2-1). Our new approach (Section 2.2.2.3) was based on activation of the 3-positions of a previously constructed bithiophene structure, followed by condensation with a source of a carbonyl group to achieve the final molecule (Route II, Figure 2-1).

Compound **2-34** (Figure 2.2) has been targeted because its four thiophene rings give the possibility of cross-linking conjugated systems in a well-defined way, with conjugation in two dimensions. Ketone **2-36** (Figure 2.2) opens the way to build copolymers of ketone **2-8** with other monomer units (section 6.1).

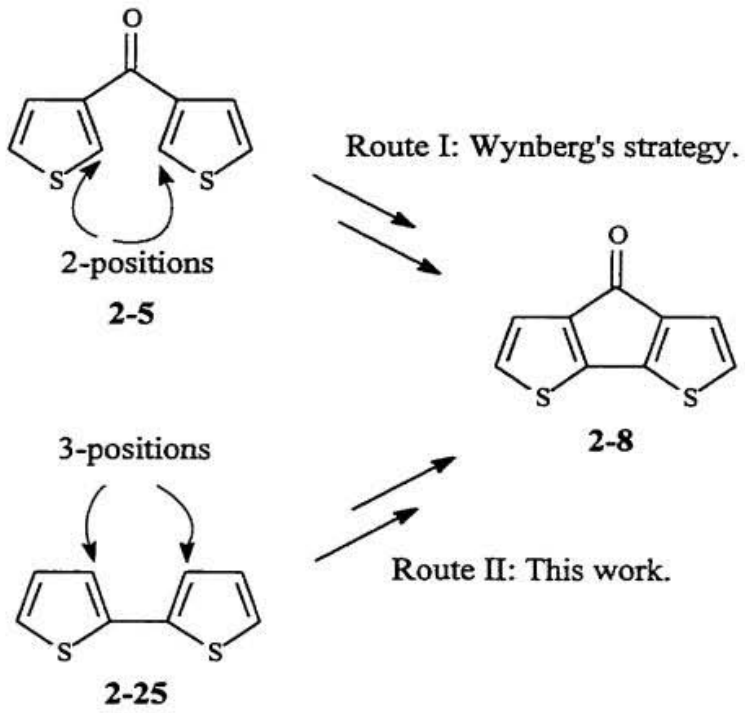


Figure 2-1. Synthetic Strategies for the Synthesis of 4*H*-Cyclopenta[2,1-*b*:3',4'-*b*']dithiophen-4-one **2-8**.

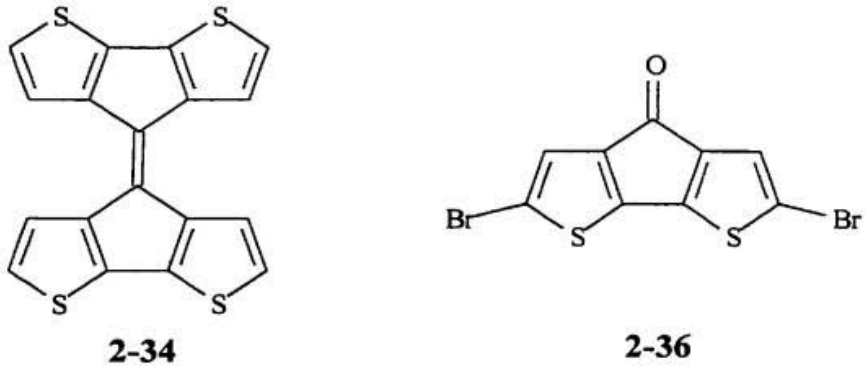


Figure 2-2. Targeted Compounds **2-34** and **2-36**

2.2 Synthesis of 4*H*-Cyclopenta[2,1-*b*:3',4'-*b*']dithiophen-4-one

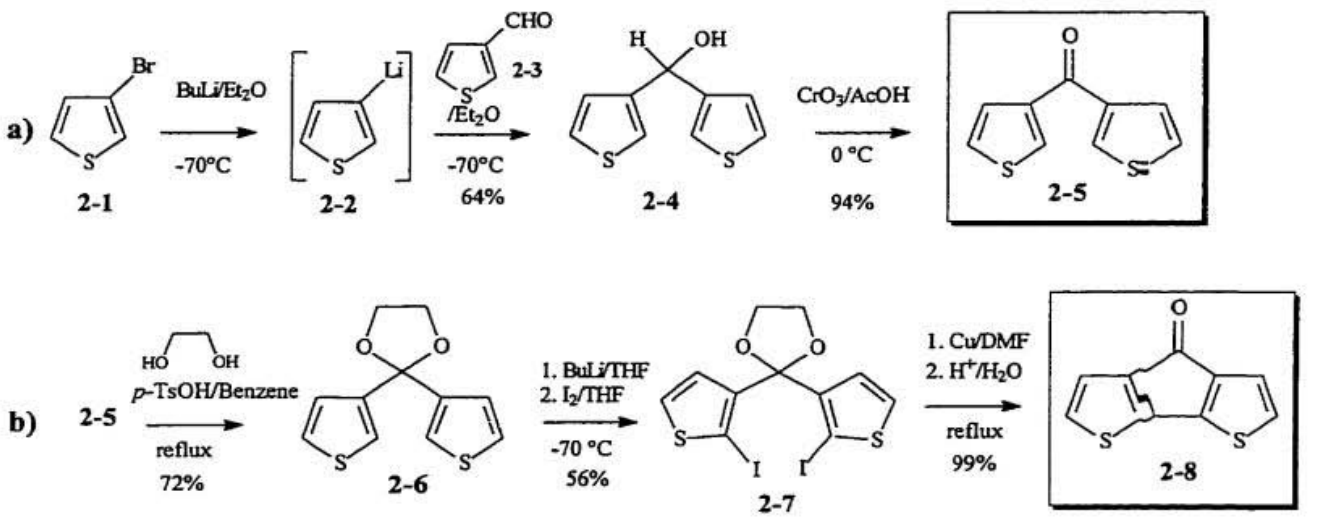
2.2.1 The Original Synthesis

The synthesis of 4*H*-cyclopenta[2,1-*b*:3',4'-*b*']dithiophen-4-one **2-8** starting from dithiophen-3-ylmethanone **2-5**, which had already been synthesized by Gronowitz and Eriksson [98] (Scheme 2-1a), was first reported in 1970 by Wynberg and coworkers [99] (Scheme 2-1b).

Gronowitz's synthesis starts with the reaction of 3-thienyllithium **2-2**, which is produced *in situ* from 3-bromothiophene **2-1** by halogen-metal exchange with *n*-butyllithium in diethyl ether at -70 °C, with 3-thiophenecarboxaldehyde **2-3** giving dithiophen-3-ylmethanol **2-4**. Oxidation of this alcohol with an aqueous acetic acid solution of chromium trioxide gives dithiophen-3-ylmethanone **2-5.**

Wynberg's synthesis involves the protection of the carbonyl as 2,2-dithiophen-3-yl-1,3-dioxolane **2-6,** using ethanediol in refluxing benzene. 2,2-Bis-(2-iodothiophen-3yl)-1,3-dioxolane **2-7** is prepared through direct metalation at the 2-positions with two molar equivalents of *n*-butyllithium and subsequent reaction with two molar equivalents of iodine. The selectivity of this reaction step may be a consequence of an ortho-directing effect of the dioxolane unit [100].

The activated 2 positions allow ring closure using an Ullmann reaction. Finally deprotection with aqueous acid during the work-up yields the desired compound **2-8.**



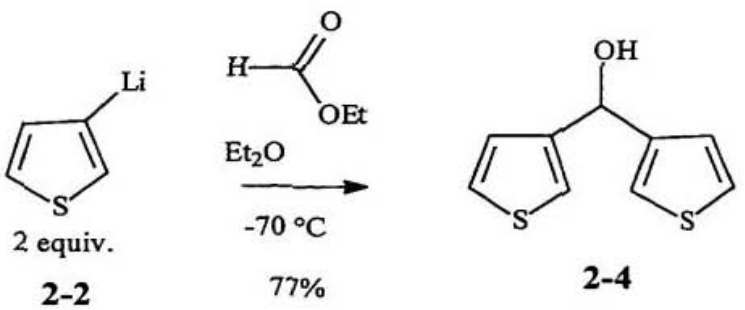
Scheme 2-1. a) Gronowitz's Synthesis of Dithiophen-3-ylmethanone.
b) Wynberg's Synthesis of 4*H*-Cyclopenta[2,1-*b*:3',4'-*b*']dithiophen-4-one.

2.2.2 Synthetic Alternatives

In spite of our successful reproduction of Gronowitz's synthesis of intermediate ketone **2-5**, an alternative synthetic methodology, avoiding expensive starting materials, such as 3-bromothiophene **2-1** and 3-thiophenecarboxaldehyde **2-3**, was one of the initial goals of this work (Section 2.2.2.1). We then found that protection of the ketone **2-5** as ketal **2-6** was problematic, with lengthy reaction times and low yields. This prompted a search for an alternative protection method (Section 2.2.2.2). Finally, it was decided that a new approach to the complete synthesis of **2-8** should be developed (Section 2.2.2.3).

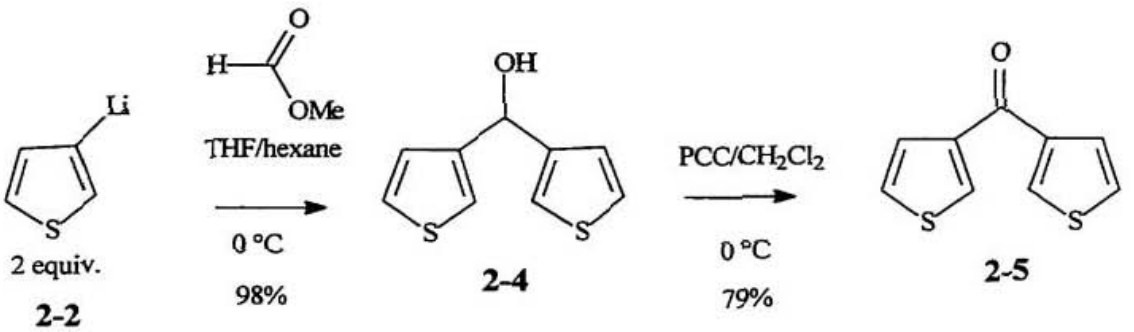
2.2.2.1 Alternative Syntheses of the Intermediate Dithiophen-3-ylmethanone

The use of 3-thiophenecarboxaldehyde can be avoided by using a different or more direct route to reach to the ketone **2-5**. For example, MacDowel and Wisowaty [101] have reported the synthesis of alcohol **2-4** (Scheme 2-2) by reaction of two molar equivalents of 3-thienyllithium **2-2**, generated from 3-bromothiophene **2-1**, with one molar equivalent of ethyl formate at -70 °C in diethylether with a reported 77% yield.



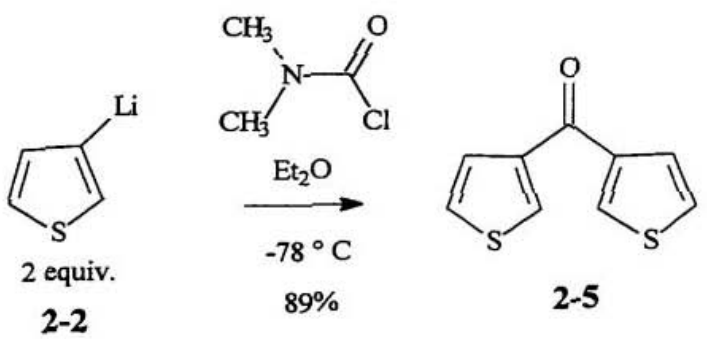
Scheme 2-2. MacDowel's Synthesis of Dithiophen-3-ylmethanol.

Williams and coworkers [102] have reported a similar preparation of alcohol **2-4** using methyl formate instead of ethyl formate, with 98% yield. Subsequent oxidation by pyridinium chlorochromate (PCC) in dry dichloromethane at 0 °C gave the ketone **2-5** in 79% yield (Scheme 2-3).



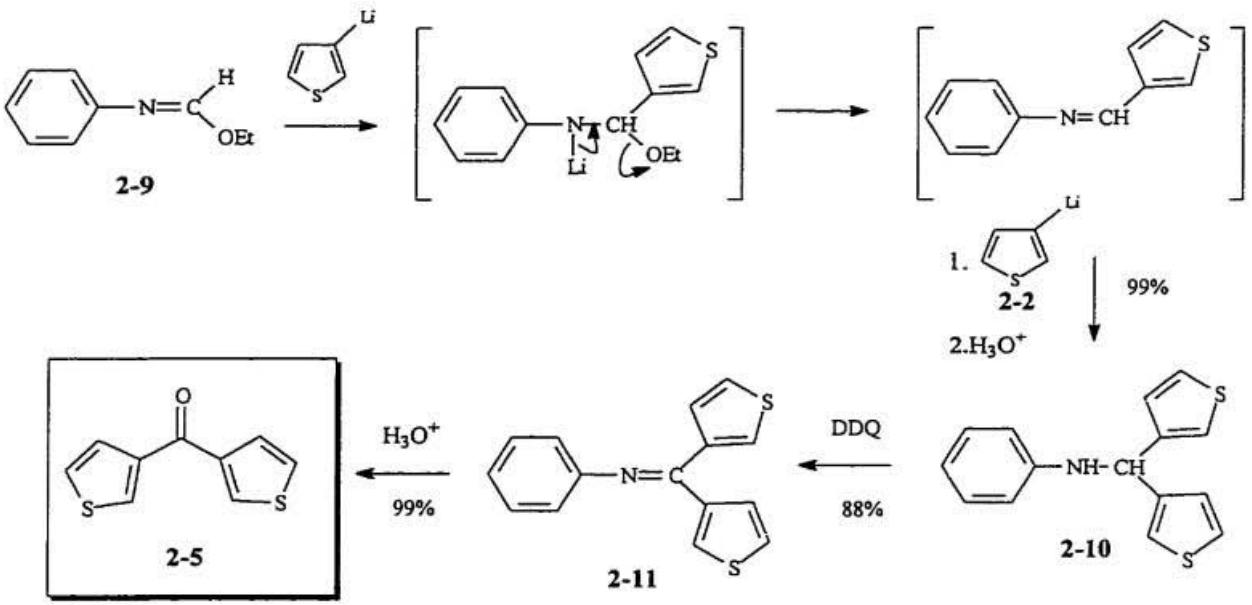
Scheme 2-3. Williams' Synthesis of Dithiophen-3-ylmethanone.

Michael and Hörnfeld [103] have investigated the reactions of several lithiated heterocycles in diethyl ether at -70 °C, including examples of 3-thienyllithium **2-2**, with *N,N*-dimethylcarbamoyl chloride and several other carbamates to afford directly the respective ketones (Scheme 2-4). The reported yields were 45% for the reaction of 3-bromothiophene **2-1** with *N,N*-dimethylethylcarbamate (Y= -OEt), 57% for *N,N*-dimethylphenyl carbamate (Y= -OPh) and 89% for *N,N*-dimethylcarbamoyl chloride (Y= Cl).



Scheme 2-4. Michael's Synthesis of Dithiophen-3-ylmethanon

Strekowsky *et al.* [104] have also reported a synthesis of ketone **2-5** (Scheme 2-5). Reaction of commercially available *N*-(ethoxymethylene)aniline **2-9** with 2 molar equivalents of 3-lithiothiophene **2-2** gave **2-10**, which was subsequently oxidized with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to Schiff base **2-11**. Hydrolysis with acid then gave the ketone **2-5** in a reported overall yield of 86% from compound **2-9.**



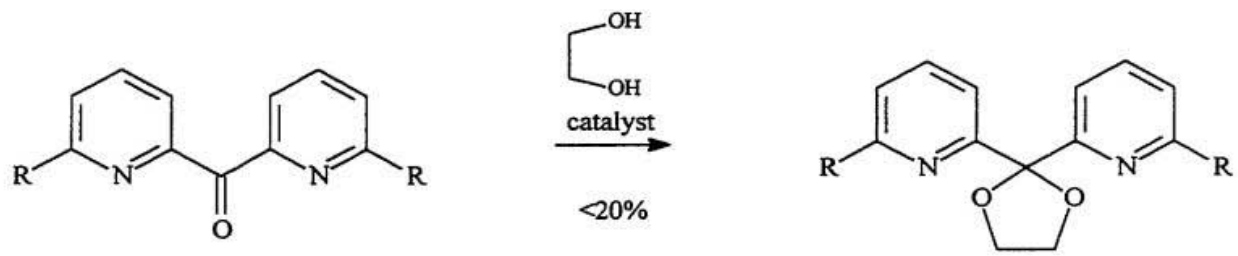
Scheme 2-5. Strekowsky's Synthesis of Dithiophen-3-ylmethanone.

Although these are all interesting approaches from a synthetic perspective, all require the use of 3-lithiothiophene **2-2**, which is generated from 3-bromothiophene.

2.2.2.2 Alternative Protection of Dithiophen-3-ylmethanone

A major problem with the original synthetic pathway to **2-8** was found to be the step in which ketal **2-6** is prepared from ketone **2-5**. After six days of reaction, TLC (silica) indicated that *ca.* 50% of ketone **2-5** remained unreacted. Moreover, a black tar, presumably a polymer, was obtained and, as a result, it was very difficult to isolate ketal **2-6** in a reasonable yield. The reaction was also carried out in higher boiling point solvents (toluene and xylene), and using different catalysts (*p*-toluenesulfonic acid or sulfuric acid), but without significant improvement.

It is noteworthy that when, during the synthesis of some heteromacrocycles, Newkome *et al.* [105] required a simple synthesis of 2,2-dipyridin-2-yl-1,3-dioxolane **2-13** (Scheme 2-6), the starting material di-pyridin-2-yl-methanone **2-12** gave poor yields of the product under diverse conditions (catalyst: *p*-toluenesulfonic acid, anhydrous hydrogen chloride, or sulfuric acid; solvent: benzene, toluene, xylene or mesitylene; temperature: 80-95 °C; time: 8-36 hours). The best experiment achieved only a 20% yield of ketal **2-13.**



2-12

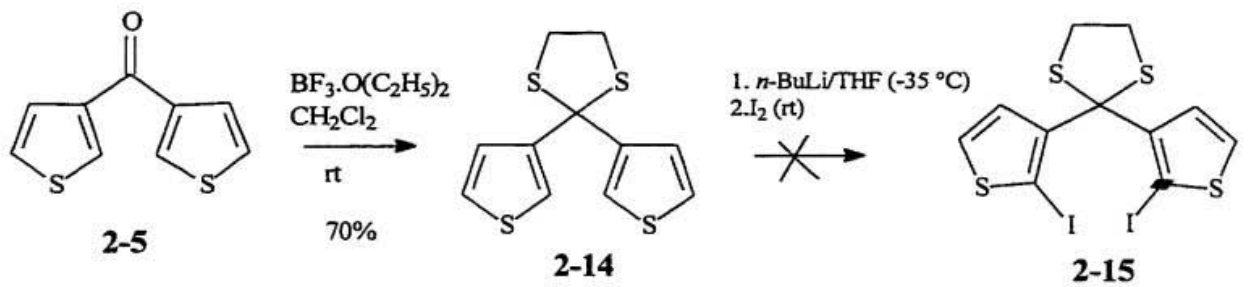
R= H or Br

2-13

Scheme 2-6. Ketalization of Dipyridin-2-ylmethanone.

There are several methods for protecting a ketone in reactions involving *n*-butyllithium. Among them, protection as a thioketal using 1,2-ethanedithiol and boron trifluoride-diethyl etherate ($BF_3.O(C_2H_5)_2$) as catalyst in dichloromethane at room temperature is widely referred to in the literature [106].

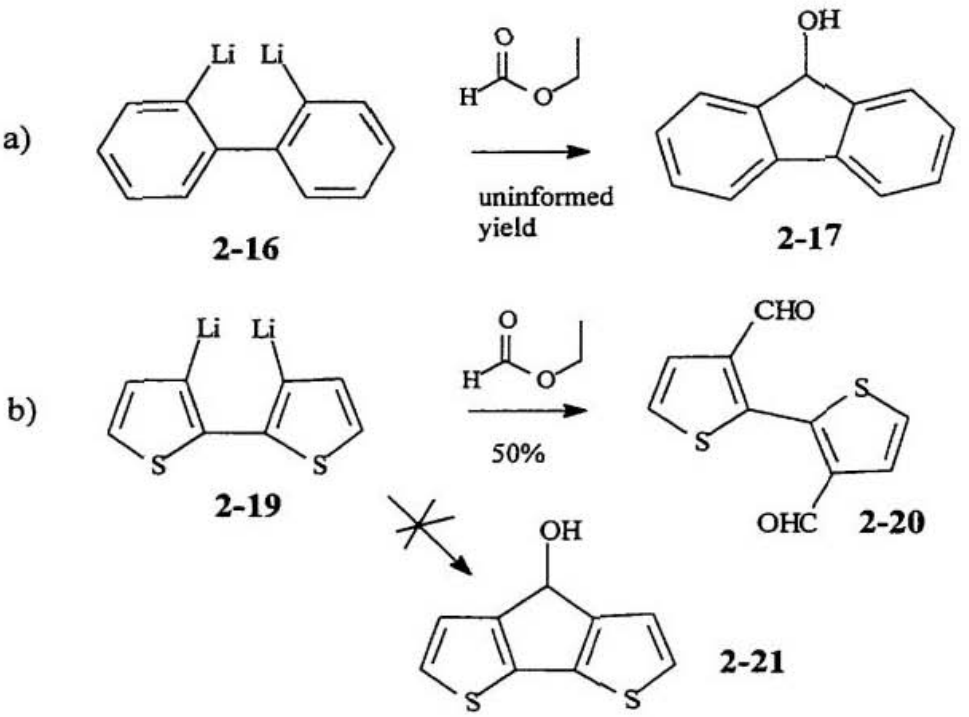
In the present case the treatment of ketone **2-5** gave 2,2-dithiophen-3-yl-1,3-dithiolane **2-14** in a reasonable yield (70%), with a shorter reaction time (18 h) than in the case of the dioxolane (6 days). Moreover, the reaction could be carried out at room temperature. Unfortunately, the next step to give 2,2-bis-(2-iodothiophen-3-yl)-1,3-dithiolane **2-15** was not successful. A black tar was produced, and no signals from the expected product **2-15** could be detected by NMR analysis of the crude product (Scheme 2-7).



Scheme 2-7. Protection of Dithiophen-3-yl-methanone as a 1,3-Dithiolane Derivative.

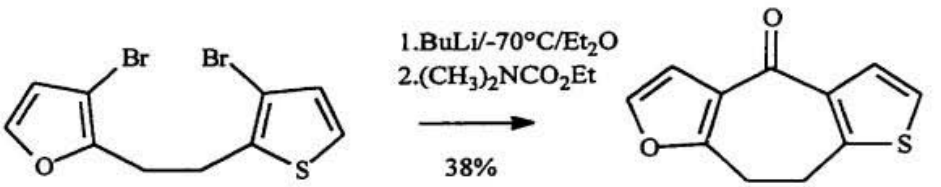
2.2.2.3 Approaches from 3,3'-Dilithio-2,2'-bithiophene

Due to the limited success of efforts to improve the original synthetic pathway previously outlined (Scheme 2-1), a different approach to the target ketone **2-8** seemed to be necessary. On the basis of the work of Adcock, who had found that reaction of 2,2'-dilithiobiphenyl **2-16** with ethyl formate leads to 9-fluorenol **2-17** (Scheme 2-8a), Gronowitz *et al.* [107] carried out the reaction of 3,3'-dilithio-2,2'-bithiophene **2-19** with ethyl formate under similar conditions. However, they obtained 3,3'-diformyl-2,2'-bithiophene **2-20** in 50% yield, instead of the expected 4*H*-cyclopenta[2,1-*b*:3',4'-*b*']dithiophen-4-ol **2-21** (Scheme 2-8b).



Scheme 2-8. a) Adcock's Synthesis of 9-Fluorenol.
b) Gronowitz's Reaction of 3,3'-Dilithio-2,2'-bithiophene with Ethyl Formate.

Several years later, Michael and Gronowitz [108] reported that the reaction between the dilithium salt of 1-(3-bromo-2-furyl)-2-(3-bromo-2-thienyl)ethane **2-22,** generated by metal-halogen exchange with *n*-butyllithium at -70°C in diethyl ether, and *N,N*-dimethylethylcarbamate gave 8,9-dihydro-4*H*-thieno[5,4-*b*']cyclohepta[1,2-*b*]furan-4-one **2-23** in 38% yield (Scheme 2-9).

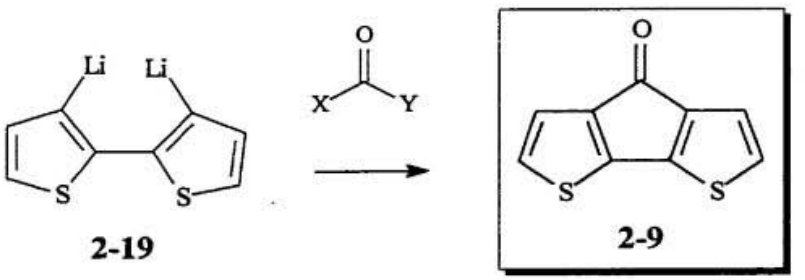


2-22 **2-23**

Scheme 2-9. Michael's Reaction of a Dibromo Heterocycle with *N,N*-Dimethylethylcarbamate.

As was discussed before (Section 2.2.2.1), Michael also reported the use of *N,N*-disubstituted carbamates and *N,N*-dimethylcarbamoyl chloride as useful reagents for the preparation of ketones from thienyllithium derivatives [103] (Scheme 2-3).

In spite of Gronowitz's failure to produce alcohol **2-21** by reaction with ethyl formate, but bearing in mind the further studies of Michael, it seemed reasonable that the reaction of 3,3'-dilithio-2,2'-bithiophene **2-19** with a suitable source of carbonyl group, such as a *N,N*-disubstituted carbamate or *N,N*-dimethylcarbamoyl chloride, might produce the desired ketone **2-8** (Scheme 2-10).



2-19 **2-9**

Scheme 2-10. Expected Reaction of 3,3'-Dilithio-2,2'-bithiophene with a Suitable Source of a Carbonyl Group.

2.2.2.3.1 Synthetic Analysis

To obtain the dilithium salt **2-19** the metalation must be by metal-halogen exchange of 3,3'-dibromo-2,2'-bithiophene **2-18** with two molar equivalents of *n*-buthyllithium, since 2,2'-bithiophene **2-25** is directly metalated to give 5,5'-dilithio-2,2'-bithiophene **2-29** [109].

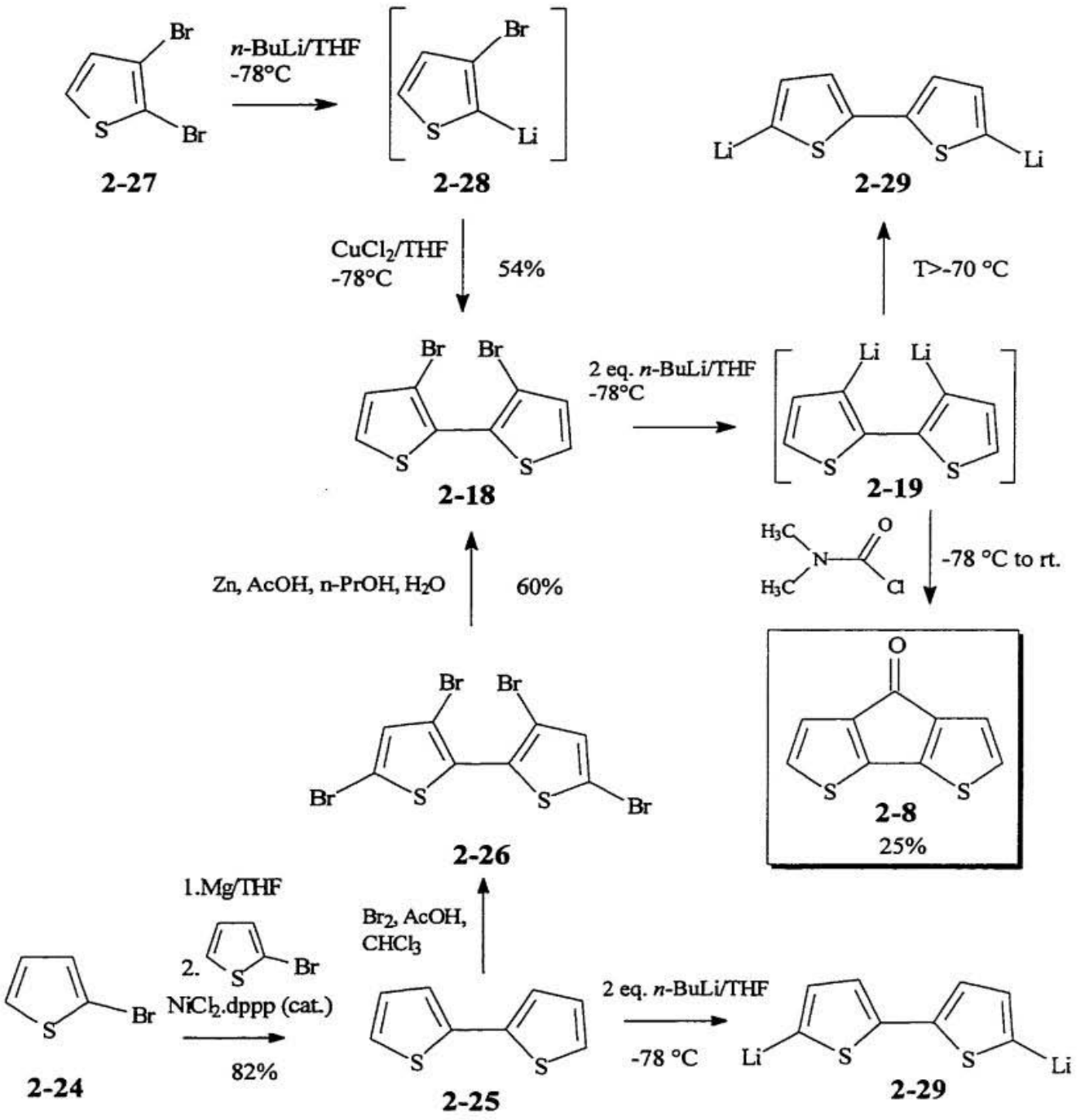
In this work two methods for the synthesis of 3,3'-dibromo-2,2'-bithiophene were tried (Scheme 2-11). First we followed Gronowitz's procedure [110], in which 2,3-dibromothiophene **2-27** was first treated with one molar equivalent of *n*-butyllithium in THF giving 3-bromo-2-thienyllithium **2-28.** The desired 3,3'-dibromo-2,2'-bithiophene **2-18** was then obtained by oxidative coupling of **2-28** with $CuCl_2$ in THF in 54% of yield. This simple procedure depends on the availability of 2,3-dibromothiophene **2-27,** which is commercially accessible, but expensive. Syntheses of 2,3-dibromothiophene **2-27** have been reported by several authors, but the starting materials are expensive (3-bromothiophene or 2,3,5-tribromothiophene) and the product itself is very difficult to purify [111-114].

A simpler alternative was reported by Khor *et al.* [115], which allows the preparation of 3,3'-dibromo-2,2'-bithiophene **2-18** from 2,2'-bithiophene **2-25,** which is not only commercially available, but also easily prepared from 2-bromothiophene **2-23** (Scheme 2-11). Thus, we prepared the Grignard compound derived from 2-bromothiophene **2-24** and then reacted it with another equivalent of 2-bromothiophene in the presence of bis(1,3-diphenylphosphino)-propane nickel(II) chloride ($NiCl_2$.dppp) as catalyst in THF to afford 2,2'-bithiophene **2-25** in 82% yield.

Reaction of 4 molar equivalents of bromine with 2,2'-bithiophene in glacial acetic acid produced 3,3',5,5'-tetrabromo-2,2'-bithiophene **2-26**, and subsequent selective debromination with Zn powder under reflux in a *n*-propanol-acetic acid-water mixture gave 3,3'-dibromo-2,2'-bithiophene **2-18** in 60% yield.

3,3'-Dilithio-2,2'-bithiophene **2-19** was obtained from 3,3'-dibromo-2,2'-bithiophene **2-20** by reaction with *n*-butyllithium at -70 °C. At higher temperatures, rearrangement to the more stable 5,5'-dilithio-2,2'-bithiophene **2-29** may occur [116], and therefore, the temperature must be mantained below -70 °C.

4*H*-Cyclopenta[2,1-*b*;3',4'-*b*']dithiophene-4-one **2-8** was finally obtained in 25% yield by reaction of 3,3'-dilithium-2,2'-bithiophene **2-19** with one molar equivalent of *N,N*-dimethyl carbamoyl chloride in THF at -78 °C. We have found that, *N,N*-dimethylethoxycarbamate and *N,N*-dimethylcarbamoyl chloride produced ketone **2-8** in similar yields (Scheme 2-10), while reaction with *N,N*-dimethylphenoxycarbamate did not produce a significant amount of ketone **2-8**.

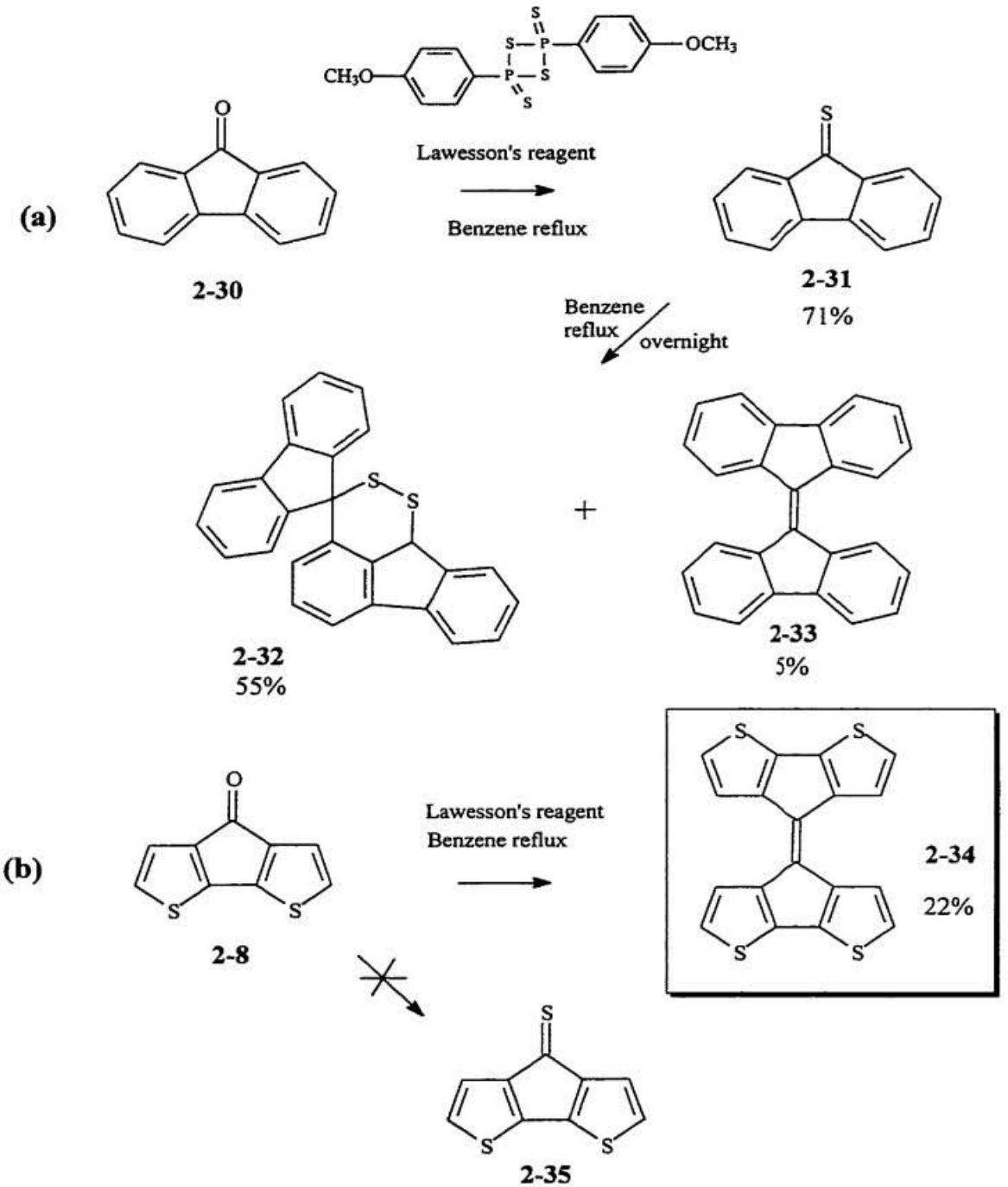


Scheme 2-11. Our Syntheses of 4*H*-Cyclopenta[2,1-*b*:3',4'-*b*']dithiophen-4-one.

2.3 Synthesis of 4*H*-Cyclopenta[2,1-*b*;3',4'-*b*']dithiophene-4-one Derivatives

2.3.1 4,4'-Bi-(4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophenylidene)

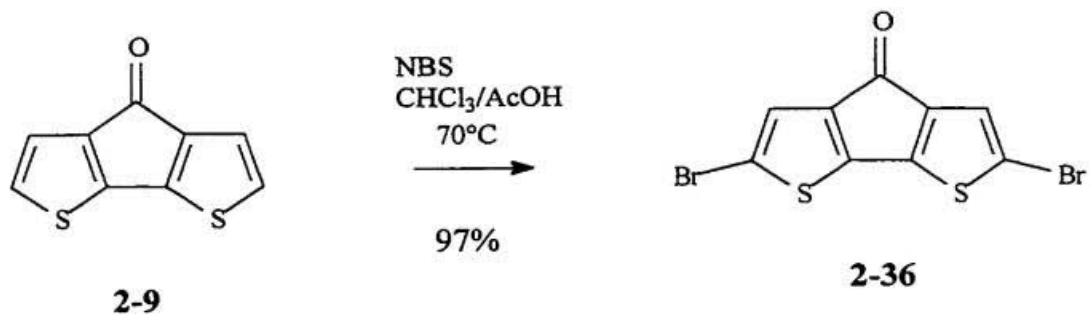
A synthesis of 4,4'-bi-(4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophenylidene) **2-34** from 4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophene-4-one **2-8** by reaction with Lawesson's reagent was developed on the basis of work reported by Scheibye *et al.* [117]. These authors obtained [9,9']bifluorenylidene **2-33** and also spiro[9*H*-fluorene-9,3'(10'b*H*)-fluoreno[9,1-*cd*][1,2]dithiin] **2-32** by reaction of 9-fluorenone **2-30** with Lawesson's reagent (Scheme 2-12a). They were also able to isolate the relatively stable 9*H*-fluorene-9-thione **2-31**. In the present case, it was not possible to detect the presence of 4*H*-cyclopenta[2,1-*b*;3',4'-*b*']-dithiophene-4-thione **2-35** intermediate, presumably due to its high reactivity, even during the early stages of the reaction (Scheme 2-12b).



Scheme 2-12. Syntheses of (a) 9,9'-Bifluorenylidene and
(b) 4,4'-Bi(cyclopenta[2,1-*b*;3',4'-*b* ']dithiophenylidene)

2.3.2 2,6-Dibromo-4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophene-4-one

The bromination of 4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophene-4-one **2-8** with *N*-bromosuccinimide (NBS) in chloroform/glacial acetic acid gave 2,6-dibromo-4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophene-4-one **2-36** in 97% yield (Scheme 2-15). Dibromide **2-36** is a promising intermediate in the synthesis of a variety of targets in which we are interested.



2-9 **2-36**

Scheme 2-13. Synthesis of 2,6-Dibromo-4*H*-cyclopenta[2,1-*b*;3',4'-*b*'] dithiophene-4-one.

2.4 Experimental

2.4.1 General procedures

Unless otherwise noted, all commercial chemicals were used without further purification. Tetrahydrofuran was distilled over sodium/benzophenone. Benzene was distilled over calcium hydride and stored over 4Å molecular sieves. Thin layer chromatography was performed on E. Merck 60 F_{254} precoated silica plates. Column chromatography was carried out on 60 (E. Merck,

230-400 mesh) silica gel. Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a General *Electric GN-300NB spectrometer at 300 MHz and 75 MHz respectively, in* $CDCl_3$ *solution* unless otherwise noted. Chemical shifts are in ppm relative to internal standard: tetramethylsilane (Me_4Si) for ^{1}H and deutero chloroform ($CDCl_3$ δ 77.0 ppm) for ^{13}C NMR. Individual signals in the ^{1}H NMR spectra are reported as chemical shift, multiplicity (s=singlet, d=doublet, dd=double doublets, t=triplet, q=quartet, m=multiplet), coupling constants and number of hydrogens. Individual signals in the ^{13}C NMR spectra are reported as chemical shift. Low resolution mass spectra (MS) were determined on a V.G. Micromass 7070HS instrument. MS data are reported as *m/z* and percent relative intensity.

24.2 2,2-Dithiophen-3-yl-1,3-dithiolane (2-14)

A solution of dithiophen-3-ylmethanone **2-5** (3.21 g, 16.5 mmol), 1,2-ethanedithiol (4.00 g, 42.4 mmol) and boron trifluoride diethyl etherate (1.5 mL , d = 1.12 g/mL, 11 mmol) in dichloromethane (60 mL) was stirred for 18 h at room temperature under a nitrogen atmosphere. The resulting reaction mixture was washed with 10% sodium hydroxide solution (4 x 75 mL), and water (4 x 100 mL). The organic layer was dried ($MgSO_4$), and solvent removed under reduced pressure to give a pale brown solid (3.50 g). The crude product was purified by column chromatography (chloroform:hexane 1:1) to afford a colorless solid identified as **2-14** (3.08 g, 11.4 mmol, 69%) (mp 60-62 °C). ^{1}H NMR δ 7.20 (m, 6H), 3.40 (s, 4H); ^{13}C NMR δ 145.7,

128.5, 126.0, 123.6, 68.5, 40.3; MS *m/z* (%) 270 (M^+, 50), 242 (32), 210 (30), 209 (22), 187 (30), 184 (22), 178 (61), 177 (100), 127 (63). Anal. calcd. for $C_{11}H_{10}S_4$: C 48.85, H 3.73, S 47.42; found C 48.82, H 3.99, S 47.19.

2.4.3 2,2'-Bithiophene (2-25) [115]

A solution of 2-bromothiophene **2-24** (33.3 g, 200 mmol) in THF (100 mL) was added under a nitrogen atmosphere to magnesium turnings (5.84 g, 240 mmol) that had been activated with a few crystals of iodine in THF (5 mL). The reaction started immediately upon the addition of a few drops of 2-bromothiophene solution, and the remaining solution was added dropwise at such a rate that the reaction mixture refluxed smoothly. When the addition was complete, a gentle reflux was maintained for 1 h. The Grignard reagent produced was cooled to room temperature and then added to a solution of 2-bromothiophene (27.6 g, 166 mmol) in THF (100 mL) containing [1,3-bis(diphenylphosphino)propane]dichloronickel(II) ($NiCl_2$dppp) (0.92 g, 1.7 mmol) at 5-10 °C over a period of 1 h. The mixture was stirred overnight at room temperature, and the resulting suspension was shaken with a saturated ammonium chloride solution (250 mL). The organic layer was collected, and the aqueous layer was extracted with diethyl ether (2 x 50 mL). The combined organic extracts were washed once with saturated sodium chloride solution (150 mL) and then dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure afforded a brown solid (30.8 g). Distillation at reduced pressure gave **2-25** as a colorless liquid (22.6 g, 136 mmol, 82%) (bp 82-84 °C/1.5 mm Hg), which solidified almost immediately

(mp 30-32 °C, lit.[29] mp 34 °C). ^{1}H NMR ($(CD_3)_3CO$) δ 7.40 (dd, J = 1.2, 5.0 Hz, 2H), 7.27 (dd, J = 1.2, 3.6 Hz, 2H), 7.07 (dd, J = 3.6, 5.0 Hz, 2H).

2.4.4 3,3',5,5'-Tetrabromo-2,2'-bithiophene (2-26) [115]

A solution of bromine (30.5 g, 191 mmol) in chloroform (230 mL) was added over 40 min to an ice-cooled solution of 2,2-bithiophene **2-25** (15.4 g, 92.7 mmol) in glacial acetic acid (300 mL) and chloroform (200 mL). To the resultant mixture was added a second portion of bromine solution (30.5 g, 191 mmol) in chloroform (230 mL) over 1 h at room temperature. The mixture was stirred overnight at room temperature and then refluxed for 24 h. It was then cooled and the solvent was removed. The solid residue (50.4g) containing **2-26** was used without further purification, although a small portion was crystallized from ethanol (mp 135-137 °C, lit.[27] mp 139-140 °C). ^{1}H NMR ($(CD_3)_2CO$) δ 7.05 (s, 2H).

2.4.5 3,3'-Dibromo-2,2'-bithiophene (2-18) [115]

To a refluxing solution of 3,3',5,5'-tetrabromo-2,2'-bithiophene **2-26** (49.8 g, 10.3 mmol) in 1-propanol (1 L), glacial acetic acid (50 mL) and water (25 mL), zinc dust was added in small portions over 5 h. After refluxing overnight, the reaction mixture was cooled and the solvent was removed. The residue was extracted with diethyl ether (3 x 100 mL) and the combined organic layers were washed with water (200 mL), saturated sodium hydrogen carbonate solution (3 x 100 mL) and saturated sodium chloride solution (150 mL). After drying ($MgSO_4$), the solvent was

removed at reduced pressure. The residue (26.3 g) was crystallized from hexanes (200 mL) giving **2-18** as colorless crystals (17.9 g, 55.3 mmol, 60% from 2,2'-bithiophene) (mp 92-95 °C, lit.[27] mp 95-97 °C). ^{1}H NMR δ 7.39 (d, J = 5.4 Hz, 2H), 7.07 (d, J = 5.4 Hz, 2H).

2.4.6 3,3'- Dibromo-2,2'-bithiophene (2-18) (Gronowitz's alternative) [110]

To a -78 °C solution of *n*-butylLithium (1.06 M in hexanes, 20.5 mL, 21.8 mmol) was added dropwise a solution of 2,3-dibromothiophene **2-27** (4.85g, 19.7 mmol) in dry THF (10 mL) under a nitrogen atmosphere. To the resulting solution of 3-bromo-2-thienyllithium was added anhydrous $CuCl_2$ (3.43 g, 25.5 mmol) and after stirring at -78 °C for 2 hours, the mixture was allowed to reach room temperature overnight. The mixture was then stirred with 20 mL of a 4 M solution of hydrochloric acid with cooling on an ice-water bath. The organic layer was washed with 4 M hydrochloric acid solution (4 x 20 mL) and water (4 x 20 mL), and then dried ($MgSO_4$). Removal of the solvent under reduced pressure gave a solid residue, which was crystallized from hexanes to yield **2-18** as light yellow crystals (1.73 g, 5.34 mmol, 54%) (mp 93-96 °C, lit.[22] mp 96-97 °C).

2.4.7 4*H*-Cyclopenta[2,1-*b*;3',4'-*b*']dithiophene-4-one (2-8)

To a -78 °C solution of 3,3'-dibromo-2,2'-bithiophene **2-18** (7.17 g, 22.1 mmol) in dry THF (100 mL) was added dropwise a solution of *n*-butyllithium (2.2 M in hexanes, 22.2 mL, 49 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 30 min and then a

solution of *N,N*-dimethylcarbamoyl chloride (2.67 g, 24.4 mmol) in dry THF (50 mL) was added dropwise over 7 hours. The resulting brown solution was maintained at –78 °C for an additional hour and then allowed to reach room temperature slowly. The mixture was stirred at room temperature overnight, and then shaken with a saturated ammonium chloride solution (100 mL). The aqueous layer was extracted with dichloromethane (2 x 100 mL), and the combined organic extracts were washed with water (100 mL) and dried ($MgSO_4$). Filtration and solvent removal by rotary evaporation afforded the crude product as a red-brown solid. Column chromatography (hexanes-chloroform 1:1) yielded **2-8** as a red-brown solid (1.17 g, 6.09 mmol, 25%) (mp 133-136 °C, lit.[11] mp 135-136 °C). ^{1}H NMR ($(CD_3)_2CO$) δ 7.35 (d, J = 4.5 Hz, 2H), 7.02 (d, J = 4.5 Hz, 2H); ^{1}H NMR δ 7.02 (d, J = 4.5 Hz, 2H), 6.97 (d, J = 4.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 182.9, 149.4, 142.6, 127.4, 121.9.

2.4.8 4,4'-Bi-(4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophenylidene) (2-34)

A solution of 4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophene-4-one **2-8** (202 mg, 1.04 mmol) and Lawesson's reagent (1.30 g, 3.12 mmol) in dry benzene was refluxed for 12 h under a nitrogen atmosphere. The reaction mixture was cooled and the solvent was then removed by rotary evaporation affording a solid, which was purified by column chromatography (hexane:dichloromethane 9:1) to give a dark brown solid (40 mg, 0.11 mmol, 22%) identified as 4,4'-bi-(4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophenylidene) **(2-34)** (mp 237-240 °C (dec)); ^{1}H NMR δ 7.52 (d, J= 5.0 Hz, 4H), 7.10 (d, J=5.0 Hz, 4H); ^{13}C NMR δ 144.7, 140.9, 125.2, 124.4, 121.4;

MS *m/z* (%) 352 (M^+, 100), 320 (7), 307 (13), 176 (14).

2.4.9 2,6-Dibromo-4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophen-4-one (2-36)

To a solution of 4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophene-4-one **2-8** (130 mg, 0.677 mmol) in 1:1 chloroform/glacial acetic acid (15 mL) was added *N*-bromosuccinimide (250 mg, 1.41 mmol) in one portion. The reaction started instantly at room temperature. The mixture was then warmed and mantained under reflux for 30 min, and then allowed to cool to room temperature. The mixture was then diluted with chloroform (50 mL) and the resulting solution was washed with 10% sodium carbonate solution (3 x 50 mL), and dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded **2-36** as a purple solid (232 mg, 0.663 mmol, 98%) (mp 202-204 °C). ^{1}H NMR δ 7.00 (s, 2H); ^{13}C NMR δ 180.7, 148.8, 139.7, 124.6, 114.2; ^{13}C NMR ($CDCl_3$, 75 MHz, gated decoupling) δ 180.7, 148.8, 139.7 ($^2J_{CH}$ = 3.6 Hz), 124.6 ($^1J_{CH}$ = 177.7 Hz), 114.2 ($^2J_{CH}$ = 2.7 Hz); MS *m/z* (%), 350 (M^+, 100), 271 (60), 269 (56), 162 (64), 117 (22), 81 (31).

Chapter 3

Synthesis

of

2,2'-(Ethyne-1,2-diyl)bis(thiophene)

Derivatives

3.1 Introduction

The insertion of ethynyl groups between thiophene units in a polythiophene structure was recently reported by Zotti *et al.* [118] and Ng *et al.* [119]. This provided an opportunity to develop new polymer structures by utilizing the reactivity of the triple bond. The following targeted structures (Figure 3-1), preserve conjugation and were expected to lead to low band gap materials.

The following sections detail the synthesis of the known compound 2,2'-(ethyne-1,2-diyl)bis(thiophene) **3-3** and two new derivatives, 4,5-dithiophen-2-yl-1,3-dithiol-2-one **3-5** and 2,3,4,5-tetrathiophen-2-yl-thiophene **3-6**.

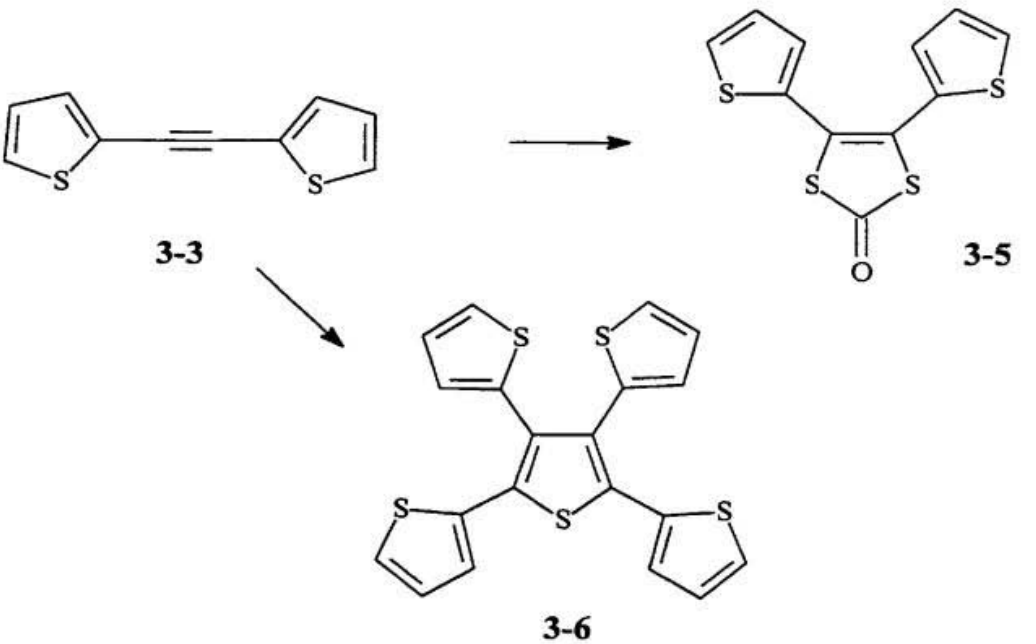


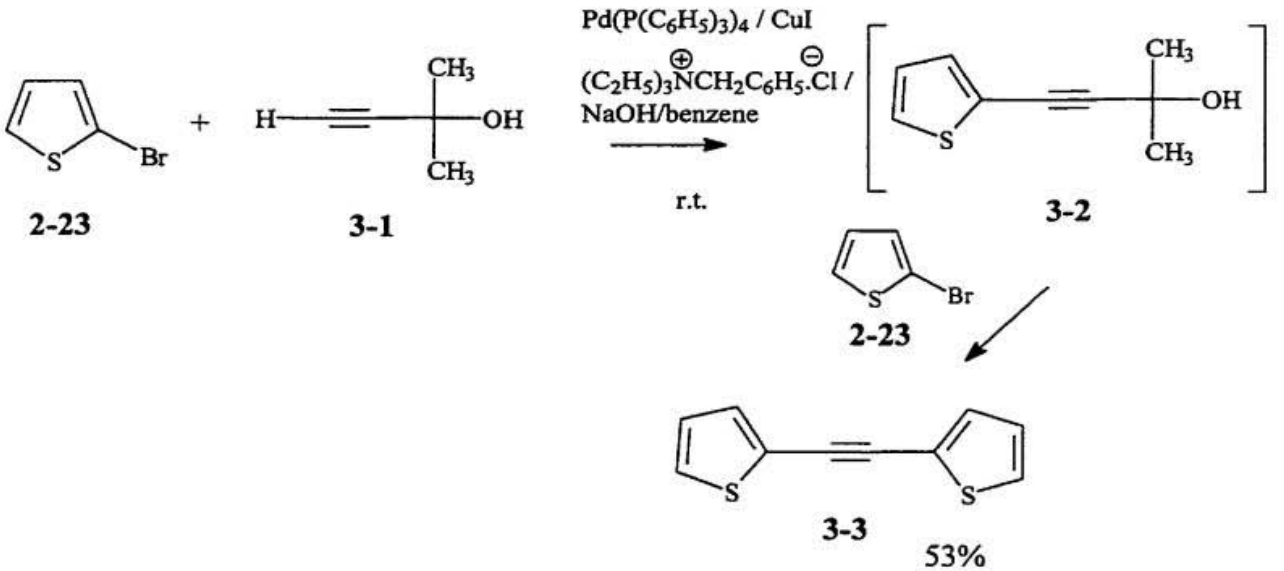
Figure 3-1. Potential Modification of the Triple Bond.

3.2 Synthesis of 2,2'-(Ethyne-1,2-diyl)bis(thiophene)

The synthetic procedure utilized in our work to give 2,2'-(ethyne-1,2-diyl)bis(thiophene) **3-3** (Scheme 3-1), was originally reported by Carpita *et al.* [120].

2-Bromothiophene **2-23** was allowed to react with one molar equivalent of 2-methyl-3-butyn-2-ol **3-1** at room temperature in the presence of tetrakis(triphenylphosphine)palladium(0) ($(C_6H_5)_3P)_4Pd$) and copper(I) iodide (CuI) as catalysts, under a nitrogen atmosphere. Aqueous 5.5 M sodium hydroxide was used as a base and, because the solvent was benzene, a phase-transfer-catalyst was necessary. In this case benzyltriethylammonium chloride ($C_6H_5CH_2N(C_2H_5)_3^+Cl^-$) was chosen.

The intermediate arylalkynol **3-2** was treated, without isolation, with another molar equivalent of 2-bromothiophene **2-23** giving the desired product **3-3** in 53% yield.

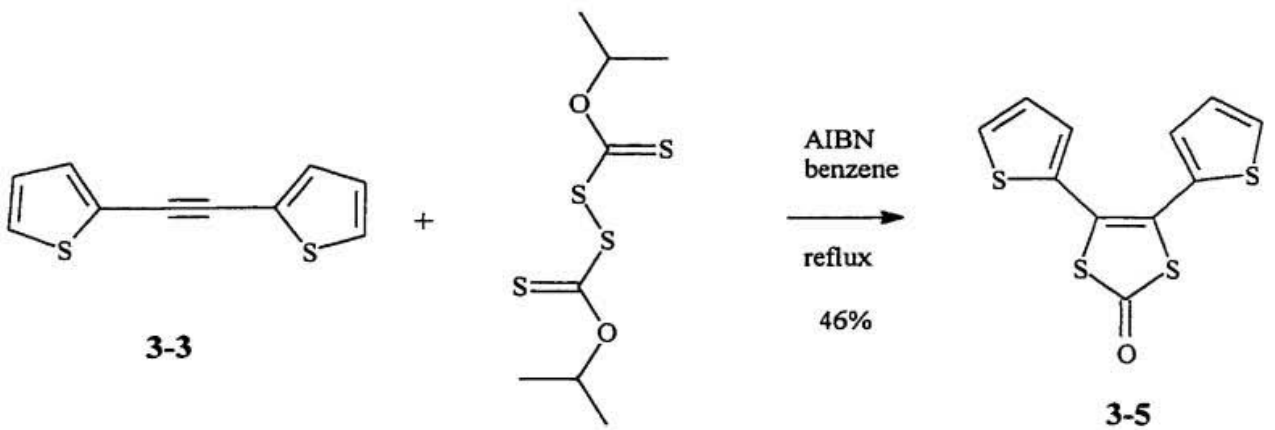


Scheme 3-1. Carpita's Synthesis of 2,2'-(Ethyne-1,2-diyl)bis(thiophene).

3.3 Synthesis of 4,5-Dithiophen-2-yl-1,3-dithiol-2-one

1,3-Dithiol-2-ones can be prepared in several ways, usually requiring many steps [121-126]. However, on the basis of the work by Gareau and Beauchemin [127], we have been able to prepare 4,5-dithiophen-2-yl-1,3-dithiol-2-one **3-5** in a single step (Scheme 3-2).

Compound **3-5** was prepared by reaction of **3-3** with 1.1 molar equivalents of the commercially available *O,O*-diisopropyldithiobis(thioformate) **3-4**, using 2,2'-azobis(2-methyl-propionitrile) (AIBN) as a free radical initiator in refluxing benzene under a nitrogen atmosphere. The resulting product **3-5** was obtained in 46% yield.



3-3 + **3-4** → **3-5**

Scheme 3-2. Synthesis of 4,5-Dithiophen-2-yl-1,3-dithiol-2-one.

3.3.1 Proposed Mechanism of the Reaction.

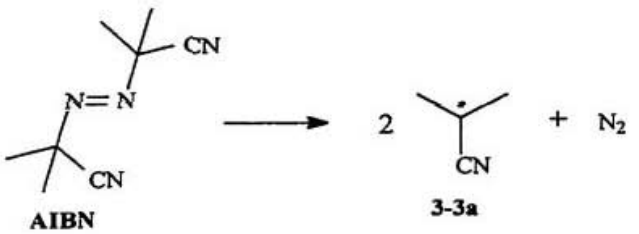
As a typical radical process, the mechanism for reaction 3-2 can be divided in three main steps (Scheme 3-3). Initiation involves the thermal decomposition of 2,2'-azobis(2-methyl-

propionitrile) AIBN to produce the radical intermediate **3-3a**, which adds the carbon-sulfur double-bond of **3-4**. Cleavage gives the radical **3-3b** and the compound **3-3c**.

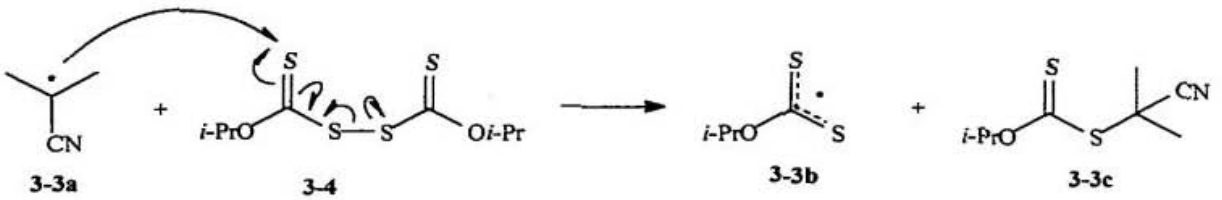
The reaction is propagated by addition of **3-3b** to the triple bond of **3-3** giving the intermediate radical **3-3d**, which by cyclization yields the desired compound **3-5** and the isopropyl radical **3-3e**. The propagation continues by another reaction of the radical **3-3e** with **3-4** regenerating **3-3b**, which continues the reaction.

Finally, termination is due to the reaction of **3-3b** with **3-3e**, giving **3-3f**, and reaction of **3-3b** with **3-3a**, giving **3-3c**. Isolation of compounds **3-3c** and **3-3f**, highlighted by Gareau and Beauchemin [127], would provide evidence for the proposed mechanism.

initiation

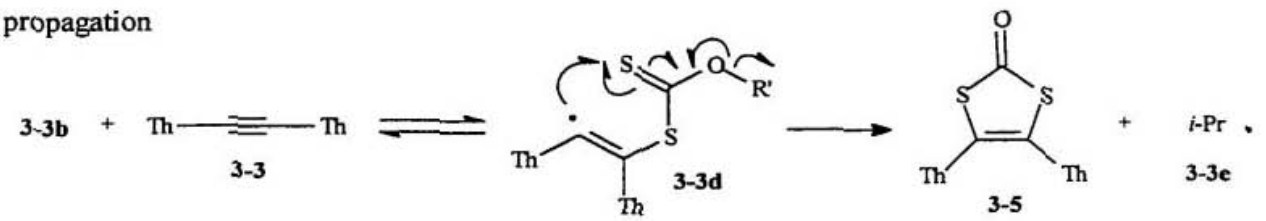


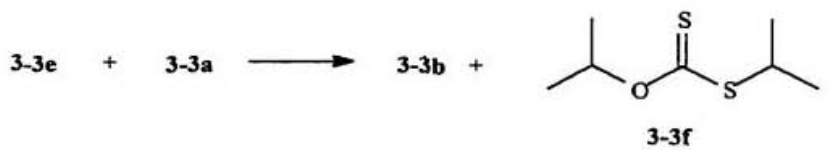
AIBN 3-3a



3-3a 3-4 3-3b 3-3c

propagation





termination

3-3b + 3-3e ⟶ 3-3f

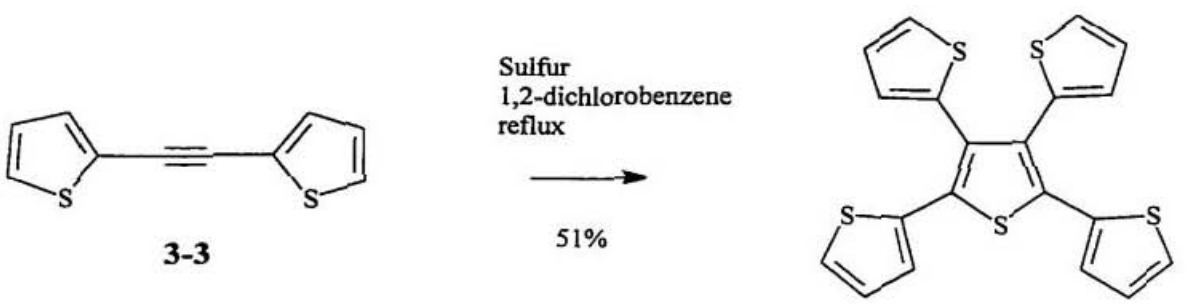
3-3b + 3-3a ⟶ 3-3c

Th = 2-thienyl

Scheme 3-3: Proposed Mechanism of Reaction for **3-2.**

3.4 Synthesis of 2,3,4,5-Tetrathiophen-2-yl-thiophene

2,3,4,5-Tetrathiophen-2-yl-thiophene **3-6** was prepared by reaction of 2,2'-(ethyne-1,2-diyl)bis(thiophene) **3-3** with 6 molar equivalents of elemental sulfur in 1,2-dichlorobenzene at reflux. Compound **3-6** was obtained in 51% yield. (Scheme 3-4).

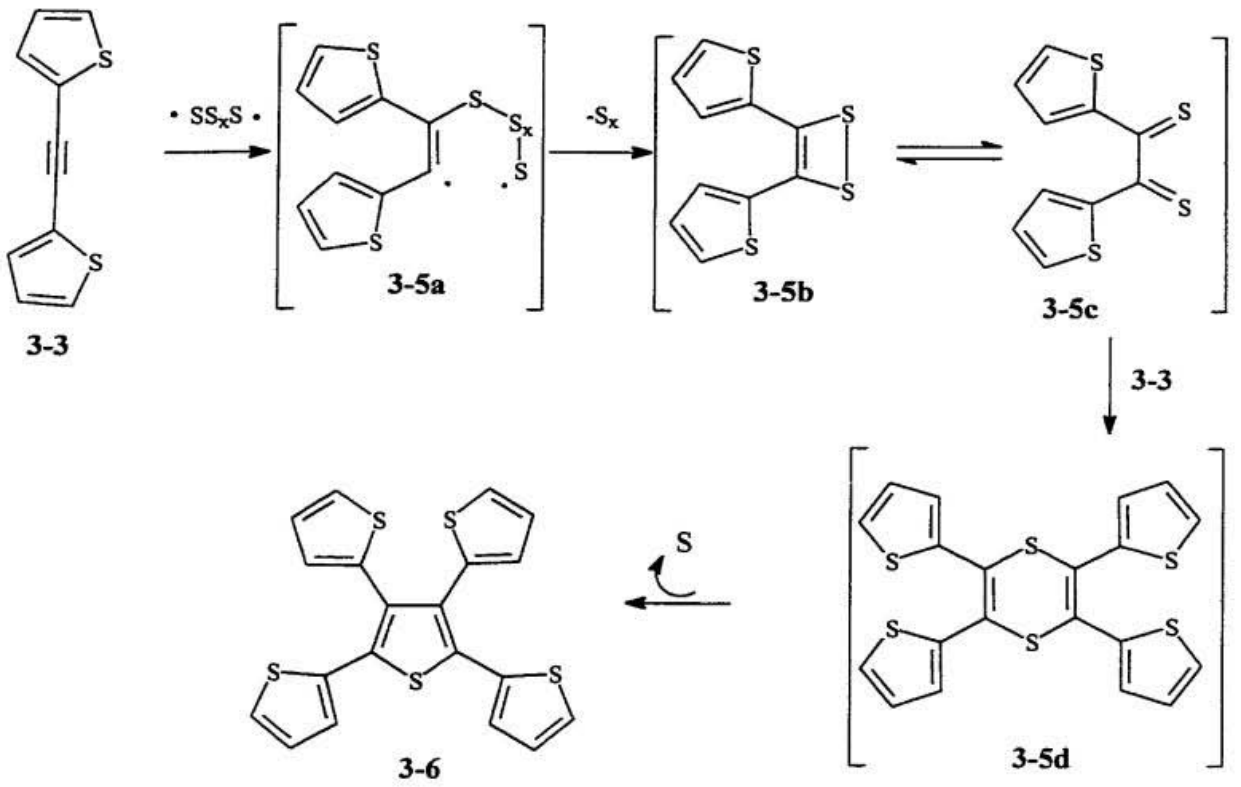


3-3 **3-6**

Scheme 3-4: Synthesis of 2,3,4,5-Tetrathiopene-2-ylthiophene.

Nakayama and coworkers [128] reported the reaction of a series of alkynes with elemental sulfur. According to the mechanism proposed by these authors, our reaction would be expected to follow the pathway shown in Scheme 3-5.

Compound **3-3** reacts with elemental sulfur giving an intermediate diradical **3-5a**, which by intramolecular cyclization with elimination of S_x affords the 1,2-dithiete **3-5b** in equilibrium with its tautomer 1,2-dithioxo compound **3-5c**. Subsequent Diels-Alder reaction of **3-5c** with the starting alkyne **3-3** would give the intermediate 1,4-dithiin **3-5d**. Finally sulfur extrusion from **3-5d** gives **3-6**.

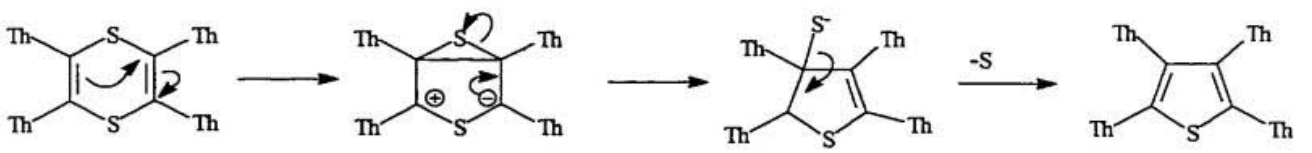


Scheme 3-5: Proposed Mechanism for the Formation of 2,3,4,5-Tetrathien-2-ylthiophene

3.5 Approach to the Synthesis of Intermediates Dithien-2-yl-1,2-dithiete (3-5b), Dithien-2-yl-1,2-dithioxo (3-5c) and 2,3,5,6-Tetrathien-2-yl-1,4-dithiete (3-5d).

Intermediates **3-5b**, its tautomer **3-5c** and **3-5d** are interesting molecules in our search for potential precursors to low band gap polymers. Our efforts were focussed on the possibility of isolating these intermediates by carrying out the reaction of **3-3** with elemental sulfur

(Scheme 3-4) at lower temperature. However, use of 1,2-dichlorobenzene over a wide range of temperatures, and benzene, toluene and xylene at reflux did not produce any evidence for the intermediates **3-5b-c** and **3-5d**. This can be explained on the basis that the initial reaction with elemental sulfur requires a high temperature. Thus, once the intermediate **3-5b** or its tautomer **3-5c** are formed, a rapid Diels-Alder reaction with the remaining starting material **3-3** produces **3-5d**, which is unstable at this temperature, suffering rapid sulfur extrusion [129] to give compound **3-6** (Scheme 3-6).

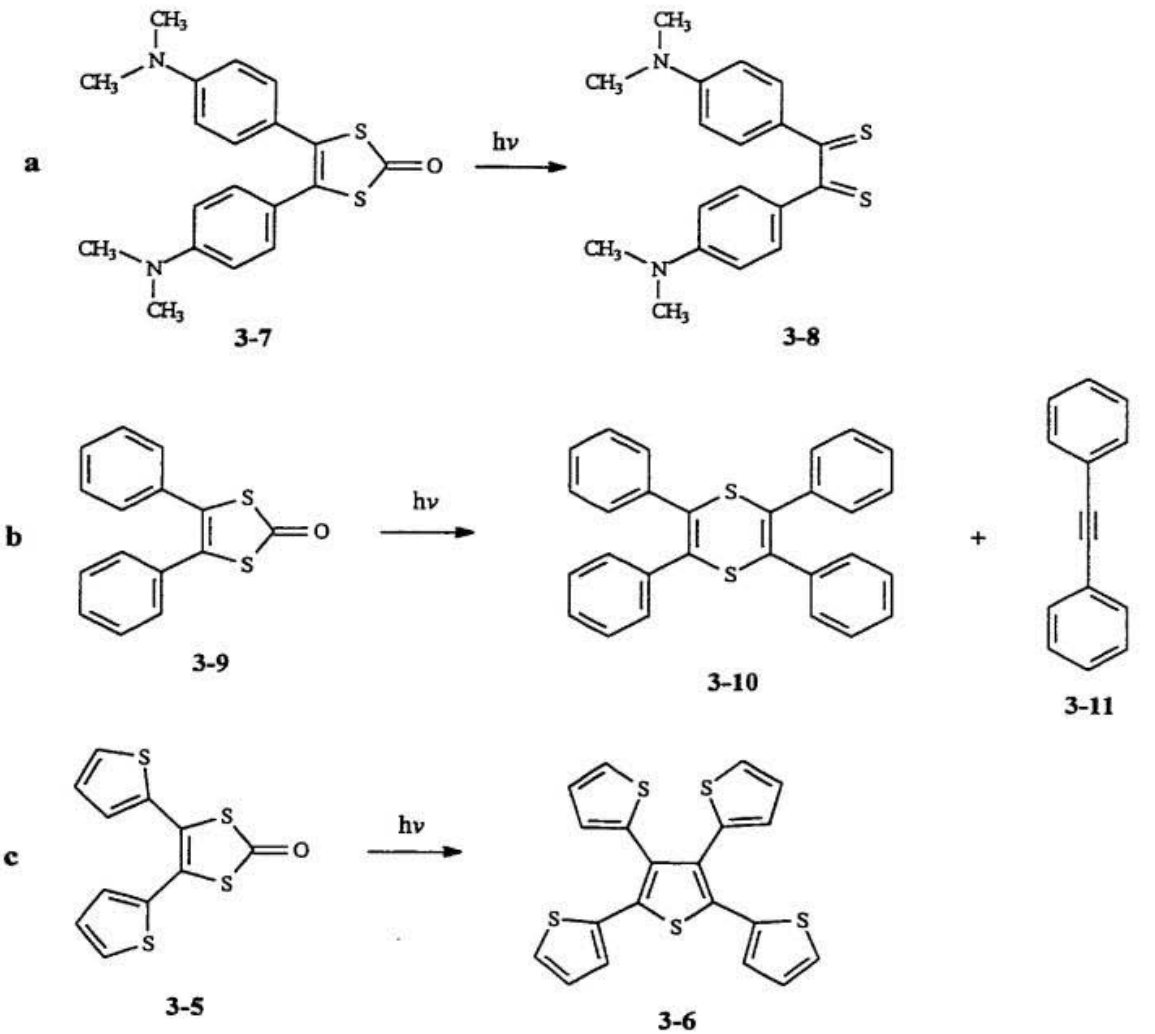


3-5d **3-5d-1** **3-5d-2** **3-6**

Scheme 3-6: Proposed Sulfur Extrusion Mechanism for 2,3,5,6-Tetrathien-2-ylthiophene.

In order to use low temperatures, our efforts focussed on the work of Kusters and de Mayo [130], who reported the isolation of di-(4-*N,N'*-dimethylaminophenyl)-1,2-dithioxo **3-8** from 4,5-di-(4-*N,N'*-dimethylaminophenyl)-1,3-dithiol-2-one **3-7** by photochemical reaction in benzene solution at room temperature (Scheme 3-7a). However, the same article reported another photochemical reaction carried out with a closely related compound, 4,5-diphenyl-1,3-dithiol-2-one **3-9**, which yielded 2,3,5,6-tetraphenyl-1,4-dithiete **3-10** as the main product with a small amount of diphenylacetylene (tolane) **3-11** (Scheme 3-7b). In our work, the photochemical

reaction of 4,5-dithienyl-1,3-dithiol-2-one **3-5** gave 2,3,4,5-tetrathienyl-thiophene **3-6** as the principal product with no evidence of the presence of any of the desired intermediates (Scheme 3-7c).



Scheme 3-7: Photochemical Reactions of 1,3-Dithiol-2-ones.

3.6 Experimental

This section follows the general procedures given in section 2.4.1

3.6.1 2,2'-(Ethyne-1,2-diyl)bis(thiophene) (3-3)

An aqueous sodium hydroxide solution (5.5 M, 45 mL), which was previously deaerated with nitrogen for 30 min, was added to a mixture of 2-bromothiophene **2-23** (10.5 g, 63.1 mmol), 2-methyl-3-butyn-2-ol **3-1** (5.40 g, 63.0 mmol), tetrakis(triphenyl-phosphine)palladium(0) ($(C_6H_5)_3P)_4Pd$) (3.26 g, 2.82 mmol), benzyltriethylammonium chloride ($C_6H_5CH_2N(C_2H_5)_3^+Cl^-$) (0.46 g, 2.0 mmol) and copper(I) iodide (CuI) (0.56 g, 2.9 mmol) in benzene (45 mL), which was previously deaerated with nitrogen for 30 min. The resulting reaction mixture, which became dark, was vigorously stirred at room temperature under a nitrogen atmosphere for 48 h. After this period of time, 2-bromothiophene (10.5 g, 63.1 mmol) in benzene (30 mL) was added to the reaction mixture, which was then refluxed for 45 h. The resulting suspension was allowed to cool to room temperature, diluted with benzene (100 mL), and then stirred with an aqueous saturated ammonium chloride solution (300 mL) for 1 h at room temperature. The aqueous layer was extracted with benzene (3 x 50 mL). The combined organic layers were dried ($MgSO_4$) and then solvent removal under reduced pressure gave a dark-brown solid. Column chromatography (hexanes) affording **3-3** as light yellow needle-shaped crystals (6.33 g, 33.3 mmol, 53%) (mp 96-98 °C, lit.[1] mp 99.5-101 °C). ^{1}H NMR δ 7.31 (dd, J = 1.2, 5.1 Hz, 2H), 7.28 (dd, J = 1.2, 3.6 Hz, 2H), 7.01 (dd, J = 3.6, 5.1 Hz, 2H); ^{13}C NMR δ 132.3, 127.8, 127.3, 123.1, 86.4.

3.6.2 4,5-Dithienyl-1,3-dithiol-2-one (3-5)

A mixture of 2,2'-(ethyne-1,2-diyl)bis(thiophene) **3-3** (1.00 g, 5.25 mmol), *O,O*-diisopropyldithiobis(thioformate) (3.60 g, 12.6 mmol), 2,2'-azobis(2-methyl-propionitrile) (0.88 g, 5.3 mmol) in dry benzene (6 mL) was refluxed under a nitrogen atmosphere for 32 h, then cooled, and the solvent was removed under reduced pressure. The brown residue was purified by column chromatography (hexanes:chloroform 2:1) and crystallization from hexanes gave **3-5** as a light brown-yellow solid (0.68 g, 2.4 mmol, 46%) (mp 90-91 °C). ^{1}H NMR δ 7.35 (dd, J = 1.2, 5.1 Hz, 2H), 7.07 (dd, J = 1.2, 3.4 Hz, 2H), 7.00 (dd, J = 5.1, 3.4 Hz, 2H); ^{13}C NMR δ 189.0, 131.9, 130.1, 128.7, 127.5, 123.0; MS *m/z* (%) 282 (M^+, 68), 254 (14), 190 (100), 127 (88), 69 (24), 45 (18). Anal. calcd. for $C_{11}H_6OS_4$: C 46.78, H 2.14, O 5.67, S 45.41; found C 46.67, H 2.25, O 5.74, S 45.19.

3.6.3 2,3,4,5-Tetrathien-2-ylthiophene (3-6)

A mixture of 2,2'-(ethyne-1,2-diyl)bis(thiophene) **3-3** (950 mg, 5.00 mmol), and sulfur (980 mg, 30.6 mmol) in 1,2-dichlorobenzene (5 mL) was refluxed for 1 h under a nitrogen atmosphere. It was cooled, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexanes:chloroform 4:1) giving a pale brown solid identified as **3-6** (0.53 g, 1.3 mmol, 52%) (mp 182-184 °C). ^{1}H NMR δ 7.29 (dd, J = 1.2, 5.1 Hz, 2H), 7.17 (dd, J = 1.2, 5.1 Hz, 2H), 7.08 (dd, J = 3.6, 1.2 Hz, 2H), 6.94 (dd, J = 5.1, 3.6 Hz, 2H), 6.92 (dd, J = 5.1, 3.6 Hz, 2H), 6.89 (dd, J = 3.6, 1.2 Hz, 2H); ^{13}C NMR δ 135.9, 135.5, 133.5, 132.6, 129.6, 127.4, 127.2, 127.1, 126. 6, 126.5; MS *m/z* (%) 412 (M^+, 42), 350 (11), 222 (22), 190 (12), 146 (15), 64 (100).

Chapter 4

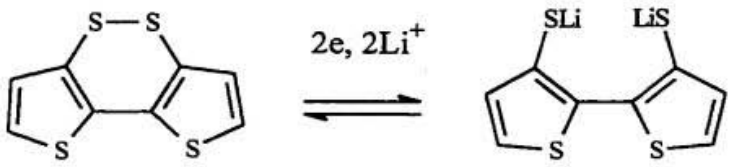
Synthesis

of

Dithieno[3,2-*c*:2',3'-*e*][1,2]dithiin

4-1 Introduction

Another objective in the present work was the synthesis of dithieno[3,2-*c*:2',3'-*e*][1,2]dithiin **4-1** and its subsequent electropolymerization. In addition to being a potential precursor for low band gap polymers, there is also the possibility of using its electrochemistry for charge storage in the cathode of a lithium (or lithium ion) battery [131]. We anticipated that the generation of the dianion would be favored by the resulting stabilization by the polymer backbone, and would involve uptake of the lithium ions generated at the anode (Figure 4-1). Our work on this type of low band gap polymer should therefore provide an entry to a class of materials with applications in batteries and supercapacitors.

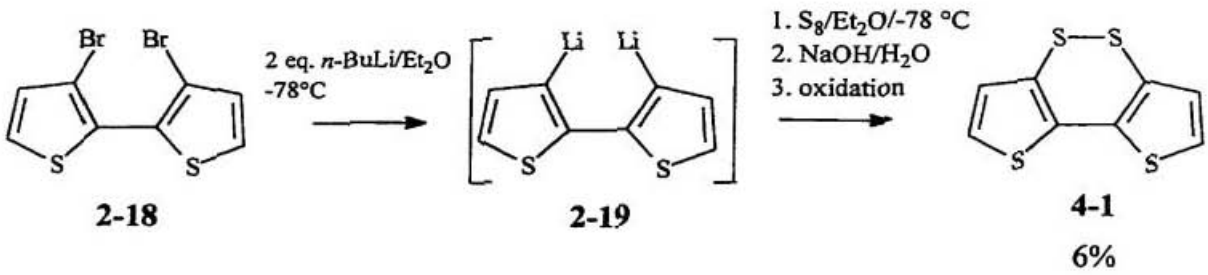


4-1 **4-1a**

Figure 4-1. Proposed Redox Equilibrium of Dithieno[3,2-*c*:2',3'-*e*][1,2]dithiin.

4.2 Synthesis of Dithieno[3,2-*c*:2',3'-*e*][1,2]dithiin

Our synthesis of dithieno[3,2-*c*:2',3'-*e*][1,2]dithiin **4-1** was based on the procedure reported by Schorth *et al.* [132] (Scheme 4-1).



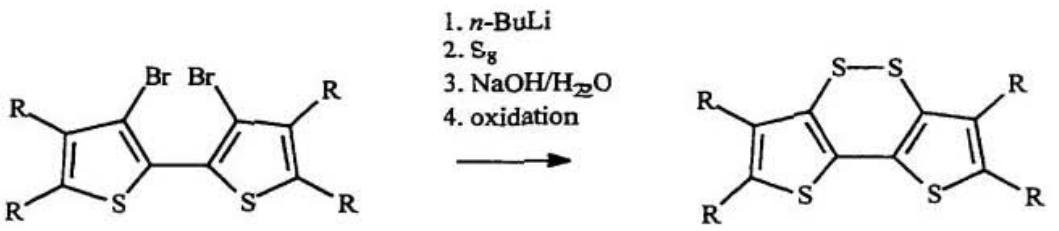
2-18 **2-19** **4-1**

6%

Scheme 4-1. Synthesis of Dithieno[3,2-*c*:2',3'-*e*][1,2]dithiin [2].

Thus, we treated 3,3'-dilithio-2,2-bithiophene, generated *in situ* from 3,3'-dibromo-bithiophene in diethyl ether at -78 °C, with elemental sulfur. The reaction mixture obtained was extracted with 10% sodium hydroxide solution and then oxidized with a 5% potassium ferricyanide solution. Following extraction with chloroform and subsequent purification by column chromatography, the desired product **4-1** was obtained in 6% yield.

The low yield obtained in this reaction is probably due to competing reactions at other positions on the thiophene rings. This is suggested by the fact that Schorth *et al.* [132] obtained significantly higher yield when using fully substituted 3,3'-dibromo-2,2'-dithiophenes (Scheme 4-2).



R= H (19%), Me (64%), Ph (61%)

Scheme 4-2. Schroth's Reaction with Substituted 3,3'-Dibromo-2,2'-bithiophenes [132].

4.3 Experimental

This section follows the general procedures given in section 2.4.1

4.3.1 Dithieno[3,2-*c*:2',3'-*e*][1,2]dithiin (4-1) [132]

To a -78 °C solution of 3,3'-dibromo-2,2'-bithiophene **2-18** (972 mg, 3.00 mmol) in dry diethyl ether (200 mL) was added dropwise a solution of *n*-butyllithium (2.3 M in hexanes, 2.8 mL, 6.4 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 30 min and then elemental sulfur (212 mg, 6.63 mmol) was added. The resulting mixture was maintained at -78 °C for an additional 3 h and then it was allowed to warm slowly to -10 °C. The mixture was treated with 10% aqueous sodium hydroxide solution (100 mL). The layers were separated, and the aqueous layer was stirred at room temperature with a 5% aqueous potassium ferricyanide

solution (80 mL) for 30 min. This aqueous layer was extracted with chloroform (2 x 100 mL), and then the combined organic extracts were washed with water (2 x 100 mL) and dried ($MgSO_4$). Solvent removal by rotary evaporation afforded the crude product as a red-brown solid. Column chromatography (hexanes-chloroform 9:1) yielded **4-1** as a red solid (0.039 g, 0.17 mmol, 6%) (m.p. 60-63°C, lit.[2] m.p 66 °C). ^{1}H NMR δ 7.25 (d, J = 5.1 Hz, 2H), 6.97 (d, J = 5.1 Hz, 2H); MS *m/z* (%) 228 (M^+, 100), 196 (44), 152 (55), 93 (51).

Chapter 5

Electropolymerization, Electrochemistry and Electronic Absorption Spectroscopy

5-1 Introduction

This chapter describes the electrochemical polymerization of the compounds synthesized in this work. The characteristics of each polymerization reaction are shown in cyclic voltammograms, and corresponding cyclic voltammograms for the resulting polymers are presented.

5.2 Experimental

Electrochemical experiments were performed in conventional three-compartment glass cells at room temperature under an argon atmosphere. The working electrode was a 0.0052 cm^2 Pt disk sealed in glass or ITO (Indium Tin Oxide) on glass (Donnelly Corp.), as specified in each figure. The reference electrode was a saturated sodium chloride calomel electrode (SSCE) and a Pt counter electrode completed the circuit.

Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (Fluka, puriss. electrochemical grade, ≥99.0%) was used without any purification. The solvents were acetonitrile (HPLC grade, distilled over dried alumina), dichloromethane (Fisher, HPLC grade, used directly), nitrobenzene (Fisher, ACS grade, distilled over $CaCl_2$ and stored over 4 Å molecular sieves).

The electrochemical measurements were carried out with Pine Instruments RDE4 and EG&G Princeton Applied Research 273A potentiostats. All data were collected and analysed using an IBM compatible microcomputer.

Spectroscopic measurements were carried out using an ITO electrode coated with the polymer with a Cary 5E UV-Vis-NIR spectrometer.

5.2.1 Poly(4,4'-Bi-(4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophenylidene)) (Poly 2-34)

Cyclic voltammograms for the growth of a film of poly-**2-34** on Pt (Figure 5-1) and for a poly **2-34** film on ITO (Figure 5-2) are shown below. The polymer exhibits a distinct oxidation peak at *ca.* +0.8 V, and a reduction peak at *ca.* -1.1 V. The *n*-doping onset and *p*-doping onset for poly **2-34** are summarized in Table 5-1 (Section 5.3). The difference between the *n*-doping onset and the *p*-doping onset (Section 1.4.3.1) provides an estimate of the HOMO-LUMO gap of the polymer.

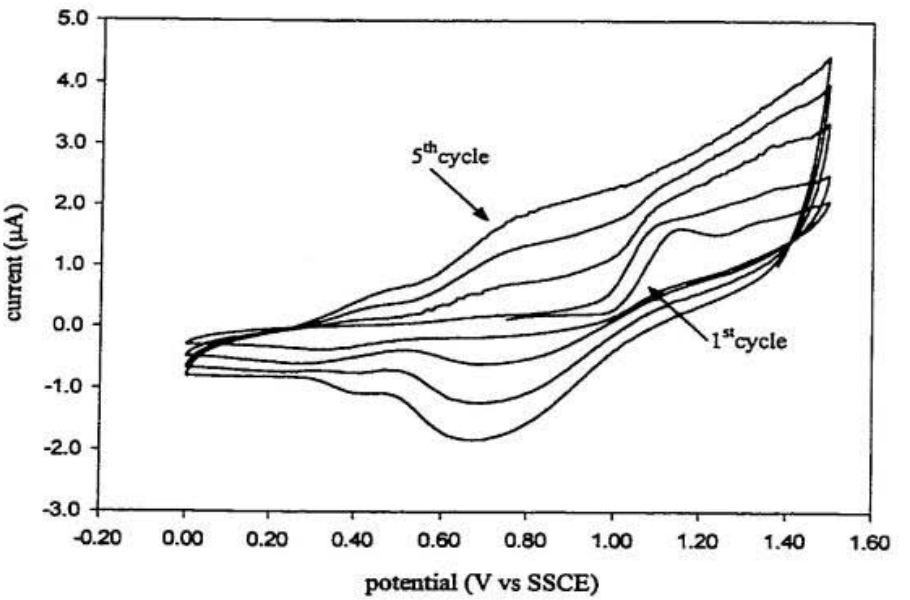


Figure 5-1. Cyclic Voltammograms for Potentiodynamic Electropolymerization of **2-34** (100 mV s^{-1} in nitrobenzene containing 0.005 M monomer and 0.01 M Bu_4NPF_6). Electrode (Pt) area: 0.052 cm^2.

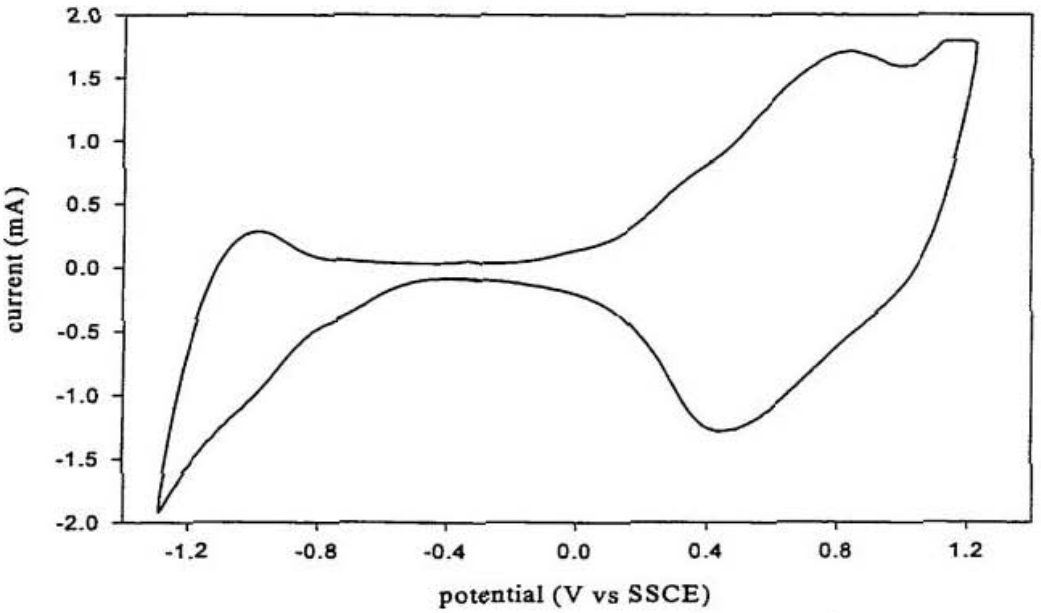


Figure 5-2. Cyclic Voltammogram (100 mV/s in acetonitrile containing 0.1 M Bu_4NPF_6) of a Poly **2-34** Film. Electrode (ITO glass) area *ca.* 2 cm^2.

The band gap of *ca.* 0.5 eV obtained for poly **2-34** is significantly smaller than the value of 1.1-1.2 eV reported for poly 4*H*-cyclopenta[2,1-*b*;3',4'-*b*']-dithiophene-4-one (poly **2-8**) [80,81]. A comparison of cyclic voltammograms of these two polymers (Figure 5-3) reveals that the decrease in band gap is caused mainly by a shift of the *p*-doping wave, indicating that poly **2-34** has a significantly higher HOMO energy.

An ITO electrode coated potentiodynamically with a layer of poly **2-34** was used for electronic absorption spectroelectrochemistry. The optical absorption onset for poly **2-34** is *ca.* 1270 nm, corresponding to a band gap of *ca.* 0.95 eV (Figure 5-4).

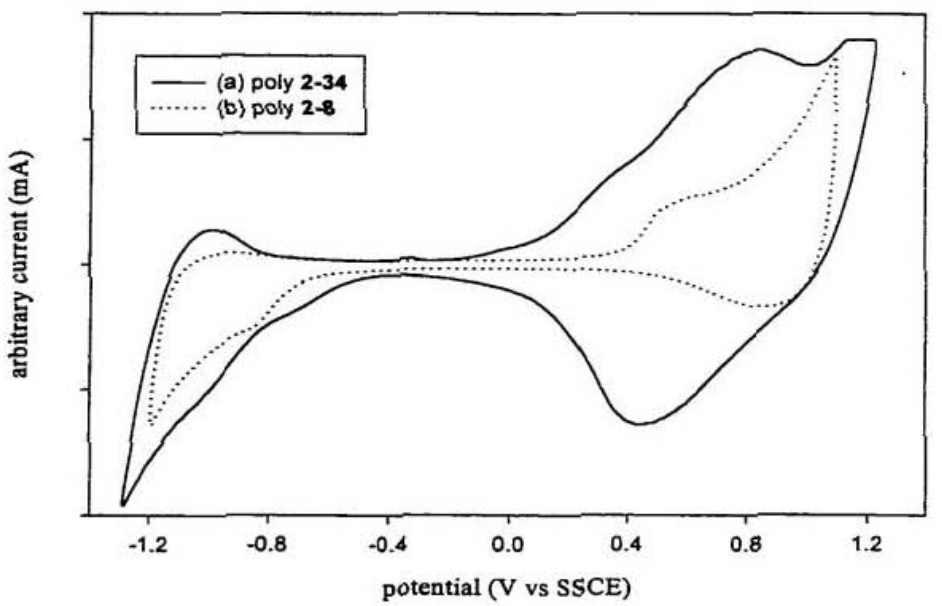


Figure 5-3. Cyclic Voltammograms (100 mV s^{-1} in acetonitrile containing 0.1 M Bu_4NPF_6) of (a) Poly **2-34** and (b) Poly **2-8** Films. Electrode (ITO glass) area *ca.* 2 cm^2.

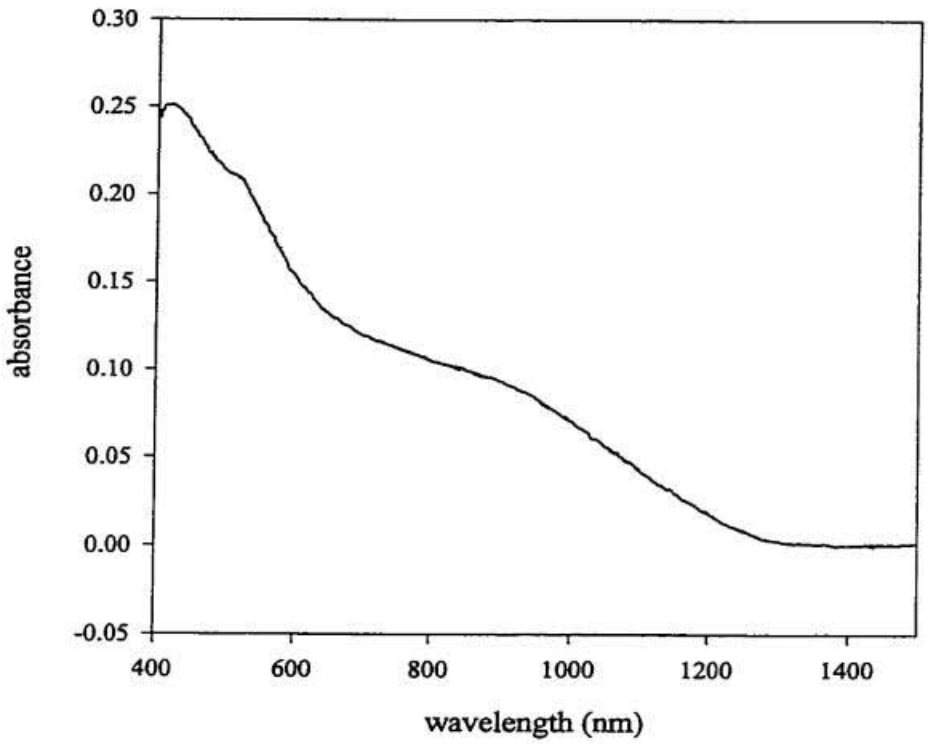
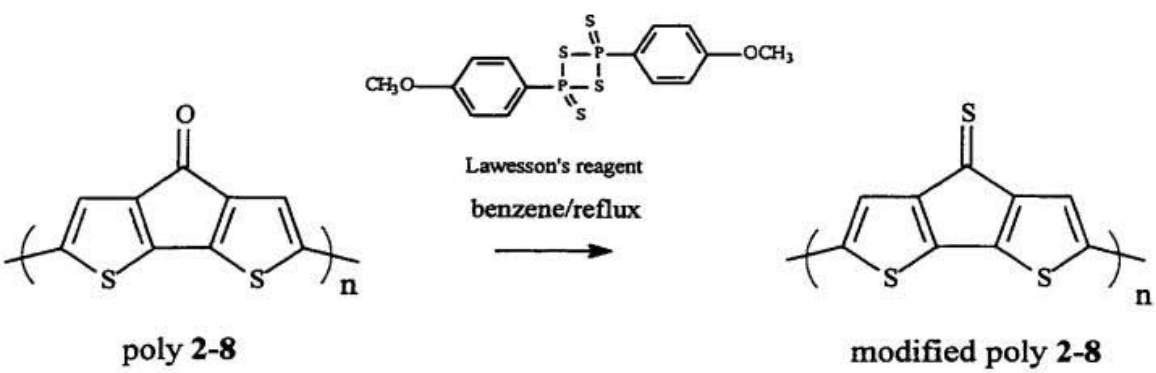


Figure 5-4. Electronic Absorption Spectrum of a Poly **2-34** Film on an ITO electrode.

5.2.2 Chemical Modification of Poly(4*H*-Cyclopenta[2,1-*b*;3',4'-*b*'] dithiophene-4-one) (Poly 2-8)

A film of poly **2-8** on ITO glass was modified by reaction with Lawesson's reagent in refluxing benzene in an attempt to prepare the thioketone as outlined below (Scheme 5-1). Cyclic voltammograms (Figure 5-5), obtained before and after modification, suggest that the band gap of the polymer has been lowered. The onset of *p*-doping is significantly earlier for the modified polymer, while other features are virtually unchanged.



poly **2-8** modified poly **2-8**

Scheme 5-1. Expected Reaction of poly **2-8** with Lawesson's Reagent.

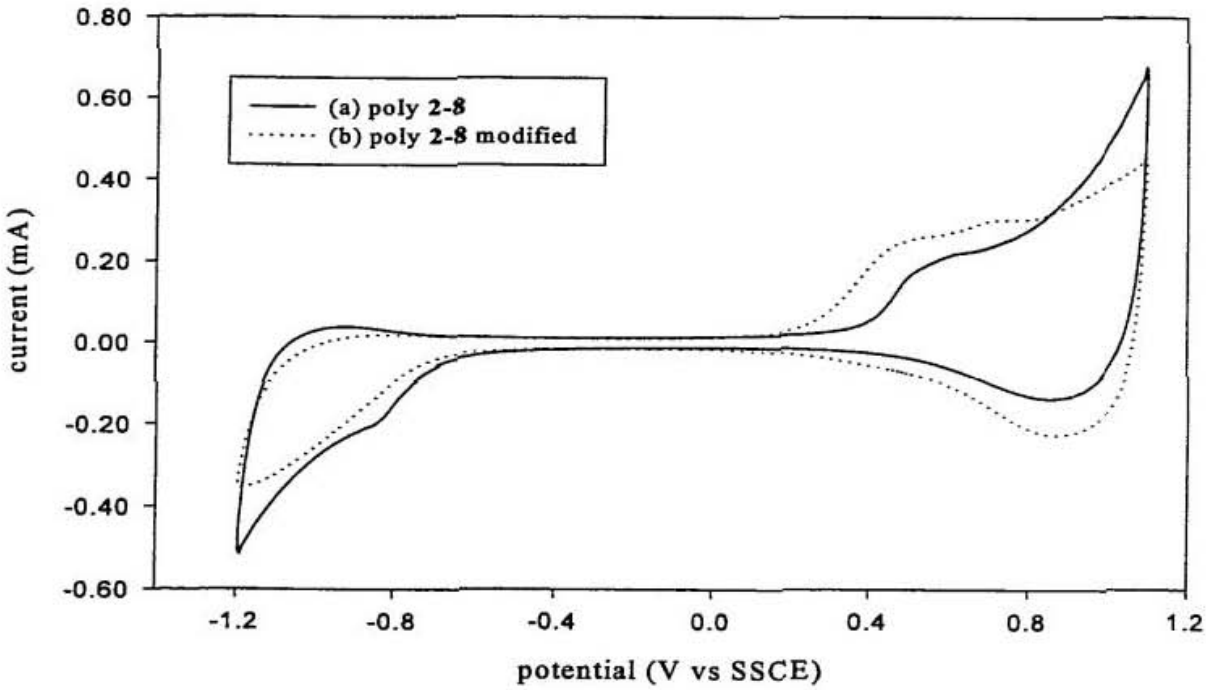


Figure 5-5. Cyclic Voltammograms (100 mV s^{-1} in acetonitrile containing 0.1 M Bu_4NPF_6) of (a) Poly **2-8** and (b) Modified Poly **2-8** Films. Electrode (ITO glass) area *ca.* 2 cm^2.

The decrease in the electrochemically determined energy gap (Table 5-1) is consistent with UV-Vis data obtained from electronic absorption spectra of the polymer films, which also show a reduction in the band gap (Figure 5-6). Further characterization of the modified film was hampered by its insolubility.

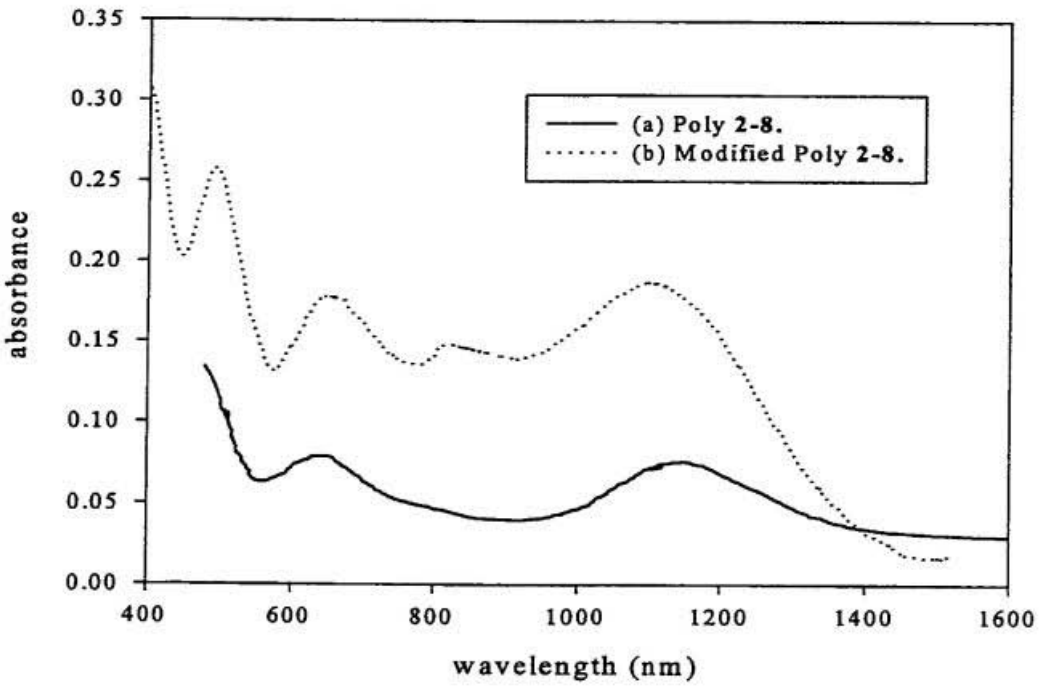
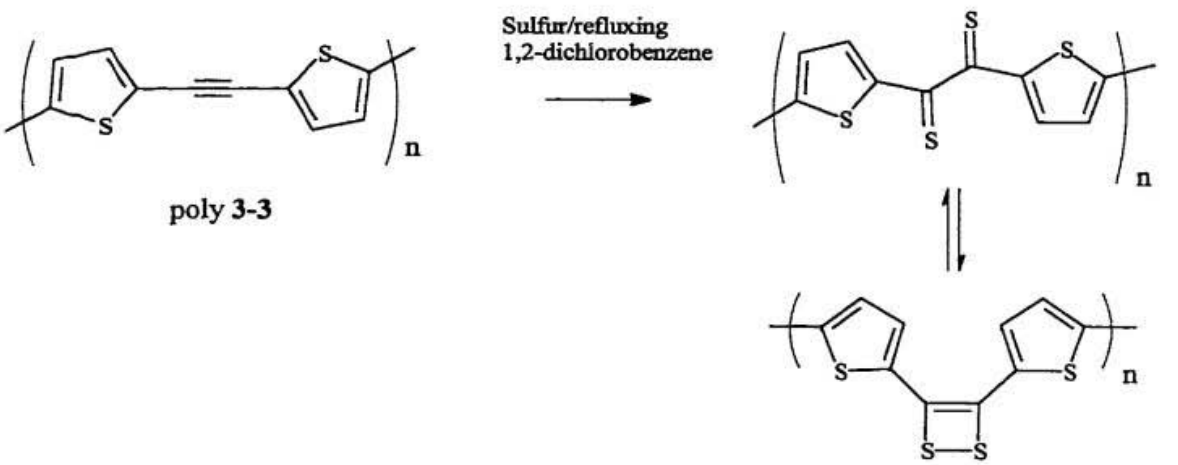


Figure 5-6. Electronic Absorption Spectra of (a) Poly **2-8** and (b) Modified Poly **2-8** Films.

5.2.3 Poly(2,2'-(Ethyne-1,2-diyl)bis(thiophene)) (Poly 3-3)

Poly **3-3** films (Figure 5-7) were prepared in order to perform *in situ* modification by reaction with elemental sulfur (Scheme 5-2). A typical cyclic voltammogram for a poly **3-3** film is shown in Figure 5-8. The UV-Vis spectroscopy performed with ITO-coated glass gave the absorption spectra shown in Figure 5-9. The optical absorption onset at *ca.* 670 nm corresponds to a band gap of 1.85 eV, which agrees not only with the cyclic voltammetric analysis (Table 5-1), but also with the literature value of 1.8 eV [119].

Reaction of films of poly **3-3** with sulfur in refluxing 1,2-dichlorobenzene under nitrogen atmosphere was expected to give a modified polymer. However, the films disintegrated during the reaction, and so it was not possible to characterize the product. The modification was also attempted with elemental sulfur in refluxing DMF. In this case, a thin polymer layer survived the reaction, but it showed no significant voltammetric or spectroscopic change from the original film.



poly **3-3**

modified poly **3-3**

Scheme 5-2. Expected Reaction of Poly **3-3** with Elemental Sulfur

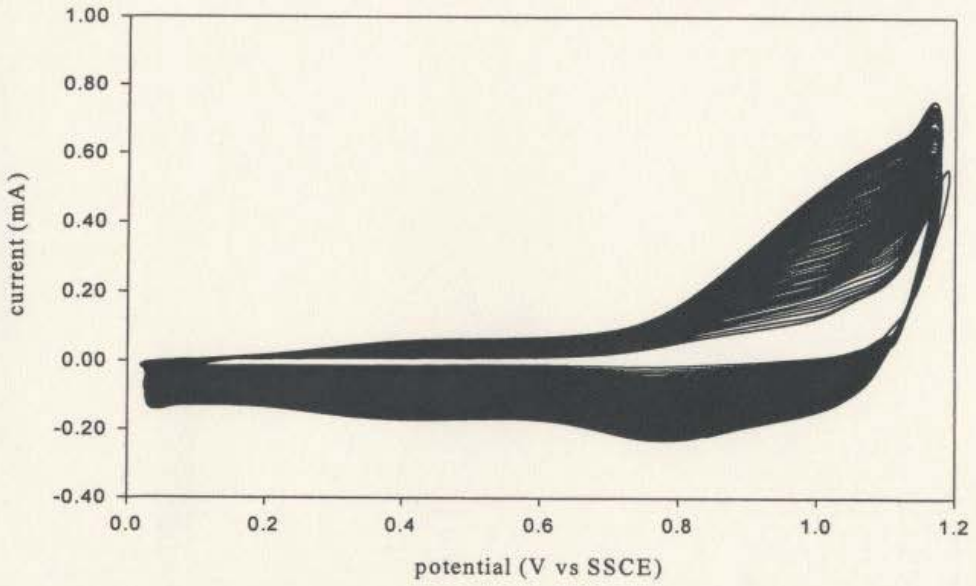


Figure 5-7. Cyclic Voltammograms for Potentiodynamic Electropolymerization of **3-3** (100 mV s^{-1} in acetonitrile containing 0.02 M monomer and 0.1 M Bu_4NPF_6). Electrode (ITO glass) area *ca.* 2 cm^{-2}.

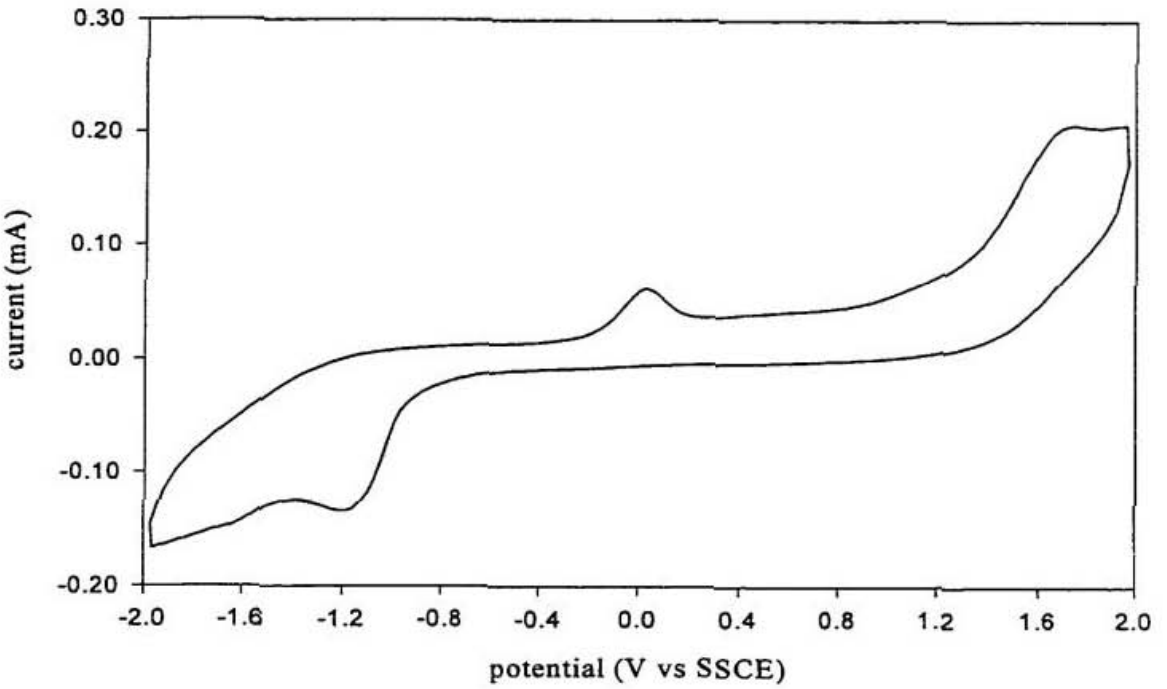


Figure 5-8. Cyclic Voltammogram (100 mV s^{-1} in acetonitrile containing 0.1 M Bu_4NPF_6) of a Poly **3-3** Film.
Electrode (ITO glass) area *ca.* 2 cm^2.

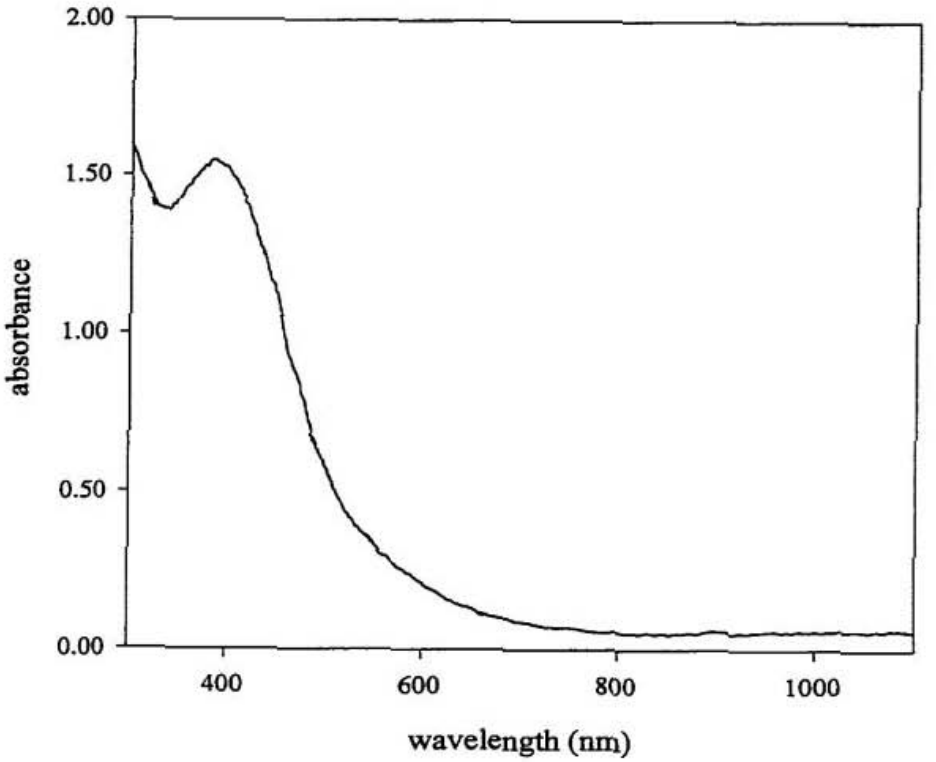


Figure 5-9. Electronic Absorption Spectrum of a Poly **3-3** Film on an ITO electrode.

5.2.4 Poly(4,5-Dithiophen-2-yl-1,3-dithiol-2-one) (Poly 3-5)

A poly **3-5** film was prepared on Pt as shown in Figure 5-10. In monomer-free electrolyte (Figure 5-11), it showed a reversible oxidation peak with a formal potential of *ca.* +0.8 V, a *n*-doping onset at *ca.* +0.6 V, and an irreversible reduction peak with an onset for the *p*-doping of *ca.* -0.9 V.

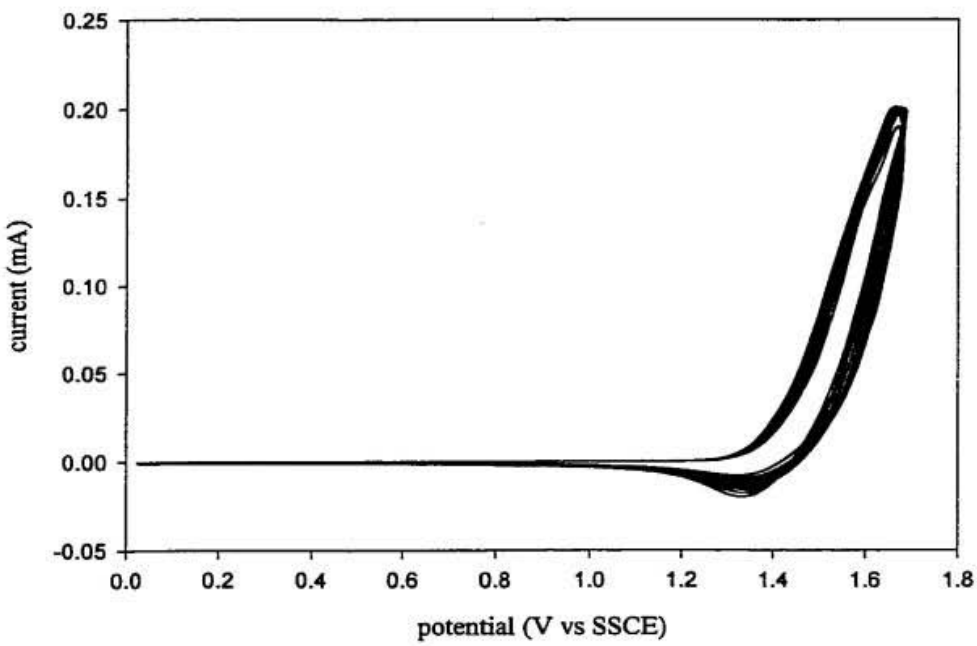


Figure 5-10. Cyclic Voltammograms for Potentiodynamic Electropolymerization of **3-5** (100 mV s^{-1} in acetonitrile containing 0.01 M monomer and 0.1 M Bu_4NPF_6). Electrode (Pt) area: 0.0052 cm^2.

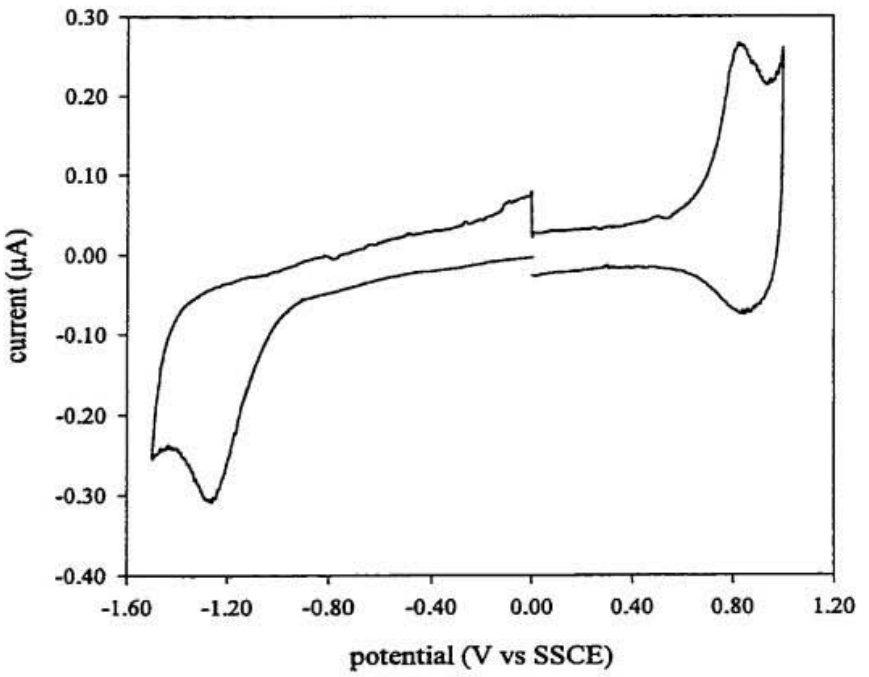


Figure 5-11. Cyclic Voltammogram (100 mV s^{-1} in acetonitrile containing 0.01 M Bu_4NPF_6) of a Poly **3-5** Film. Electrode (Pt) area: 0.0052 cm^2.

Electronic absorption spectroscopy of an ITO electrode coated by potentiodynamic electropolymerization of **3-5** (Figure 5-12) showed an optical absorption onset at *ca.* 770 nm (1.6 eV) in good agreement with the electrochemical measurements.

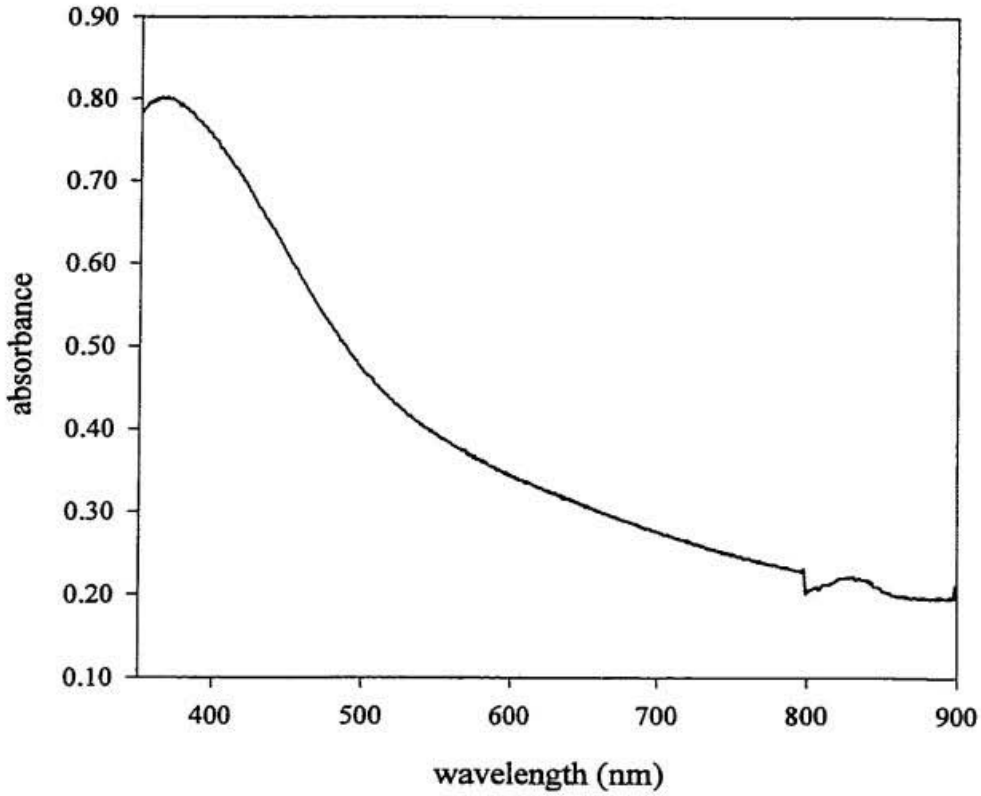


Figure 5-12. Electronic Absorption Spectrum of a Poly **3-5** Film on an ITO Electrode.

5.2.5 Poly(Tetrathien-2-ylthiophene) (Poly 3-6)

A poly **3-6** film was prepared on a Pt electrode as shown in Figure 5-13. A cyclic voltammogram for the resulting poly **3-6** is given in Figure 5-14, showing a reversible oxidation peak with a formal potential of *ca.* +0.8 V, and a reversible reduction peak with a formal potential of *ca.* -1.7 V. The band gap for this polymer (1.9-2.0 eV) was only estimated by cyclic voltammetry, because it was impossible to coat a film onto an ITO electrode.

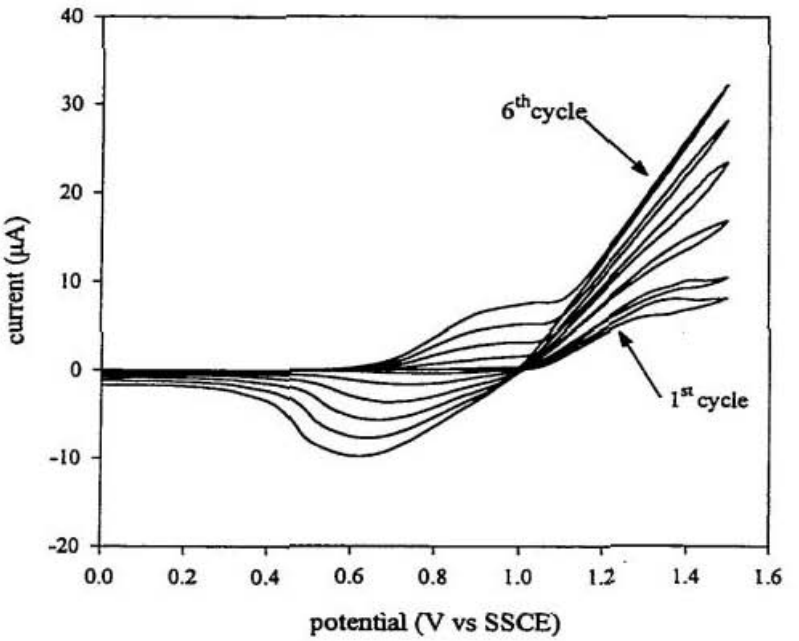


Figure 5-13. Cyclic Voltammogramms for the Potentiodynamic Electropolymerization of **3-6** (100 mV s^{-1} in dichloromethane containing 0.005 M monomer and 0.01 M Bu_4NPF_6). Electrode (Pt) area: 0.0052 cm^2).

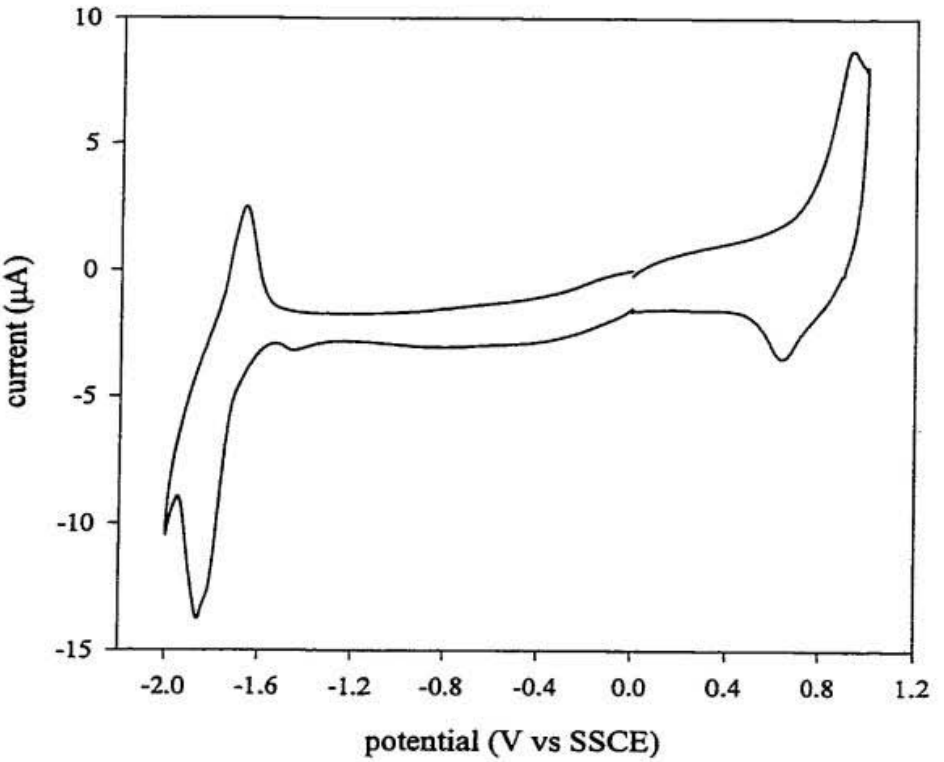


Figure 5-14. Cyclic Voltammogram (100 mV s^{-1} in dichloromethane containing 0.01 M Bu_4NPF_6) of a Poly **3-6** Film.
Electrode (Pt) area: 0.0052 cm^2.

5.2.6 Poly(Dithieno[3,2-*c*:2',3'-*e*][1,2]dithiin) (Poly 4-1)

A poly **4-1** film was prepared on Pt (Figure 5-15). It exhibited (Figure 5-16) a formal potential for reversible oxidation at *ca.* + 1.0 V vs SSCE and formal a potential for reversible reduction at *ca.* - 1.8 V vs SSCE. There appears to be no evidence for electrochemical activity of the disulfide bridge.

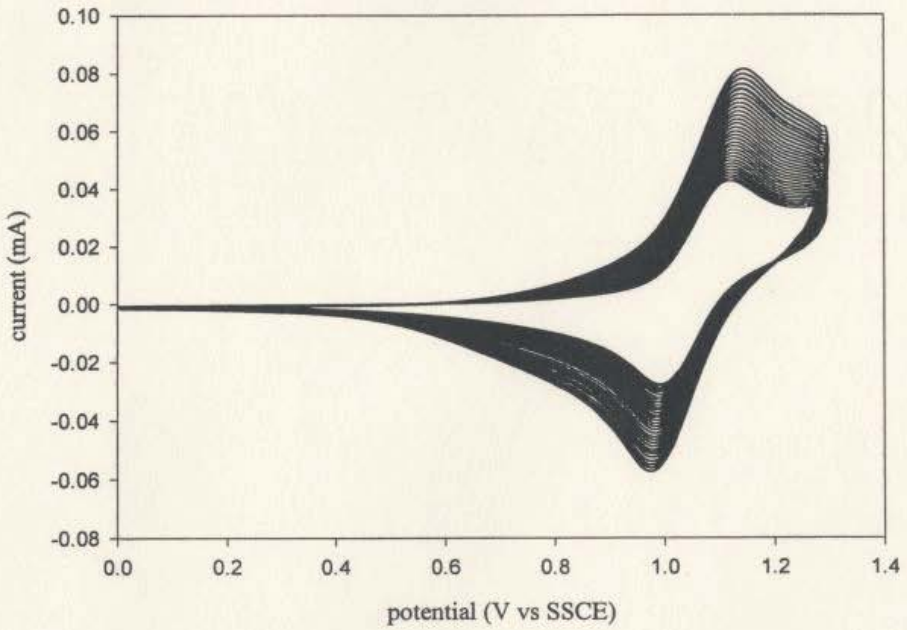


Figure 5-15. Cyclic Voltammograms for Potentiodynamic Electropolymerization of **4-1** (100 mV s^{-1} in acetonitrile containing 0.01 M monomer and 0.1 M Bu_4NPF_6). Electrode (Pt) area: 0.0052 cm^2.

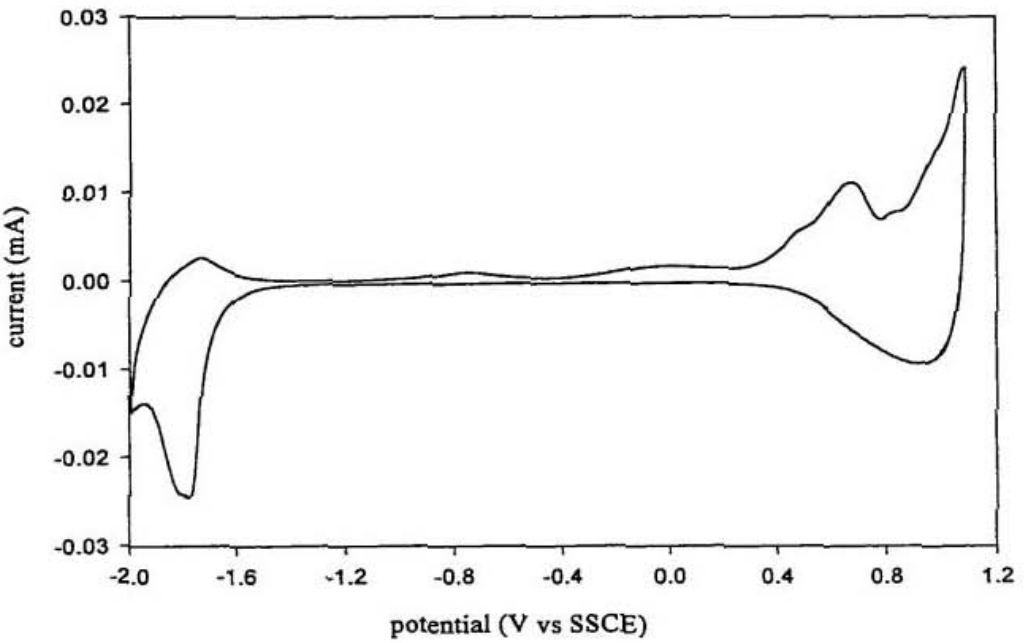


Figure 5-16. *Cyclic Voltammogram (100 mV s^{-1} in acetonitrile containing 0.1 M Bu_4NPF_6) of a Poly* **4-1** *Film. Electrode (Pt) area: 0.0052 cm^2.*

5-3 Summary of Electrochemical and Electron Absorption Spectroscopy.

The results from this chapter are summarized in Table 5-1. The agreement among the results from the electrochemical analysis and the spectroscopy, as well as with literature values where available (poly **2-8** and poly **3-3**) is quite remarkable. It can be seen from the data that we have prepared two notable new low band gap polymers, poly **2-34** (0.5-0.9 eV) and modified poly **2-8** (0.8-1.0 eV).

Table 5-1. *n*-Doping and *p*-Doping Onset Potentials, Electrochemical and Optical Band Gaps from Electronic Absorption Spectroscopy and Cyclic Voltammetry.

Polymer	Potential (V vs SSCE)		Electrochemical Gap (eV)	Optical Gap (eV)
	n-doping onset	*p*-doping onset		
2-34	+0.6	0.0	0.5-0.6	0.9
2-8	+0.4	-0.7	1.1-1.2[a]	1.0
Modified **2-8**	+0.2	-0.8	0.9-1.0	0.8
3-3	+1.1	-0.9	1.9-2.0[b]	1.9
3-5	+0.6	-0.9	1.5	1.6
3-6	+0.4	-1.6	2.0-2.1	
4-1	+0.9	-1.6	2.4-2.5	

a) Lit. [80,81] 1.1-1.2 eV. b) Lit. [119] 1.8 eV.

Chapter 6

Future Work

6.1 Future Work

Research and interest in the interdisciplinary field of conducting polymers have grown explosively since its beginnings just 20 years ago. The disciplines explored during our research were organic synthetic chemistry and the use of electrochemical techniques for driving polymerization reactions and characterization (CVs) of the resulting polymers. The work presented in this thesis is the starting point for the development of many new materials. Compound **2-34** has been shown to produce polymer with surprisingly high intrinsic conductivity that has been attributed to the presence of conjugated crosslinks [133]. It is anticipated to be a useful unit for producing low band gap crosslinked copolymers.

Compound **3-5** is of interest as a precursor to the expected low band gap polymer poly **6-3** [134] (figure 6-1). Possible routes to **6-3** and poly **6-3** include: preparation of salt **6-1** from **3-5** and then direct polymerization to poly **6-1** and neutralization to achieve poly **6-2**, or neutralization to the dithiol **6-2** and the polymerization to obtain poly **6-2**. Compound **6-2** can be oxidized to dithioketone **6-3** and then polymerization or direct oxidation of poly **6-2** (Figure 6-1b). The redox chemistry of poly **6-1** - poly **6-2** (Figure 6-1b highlighted) may be of value for charge storage batteries.

Compound **2-36** is an useful monomer for a wide range of low band gap copolymers (Figure 6-1 c [135]).

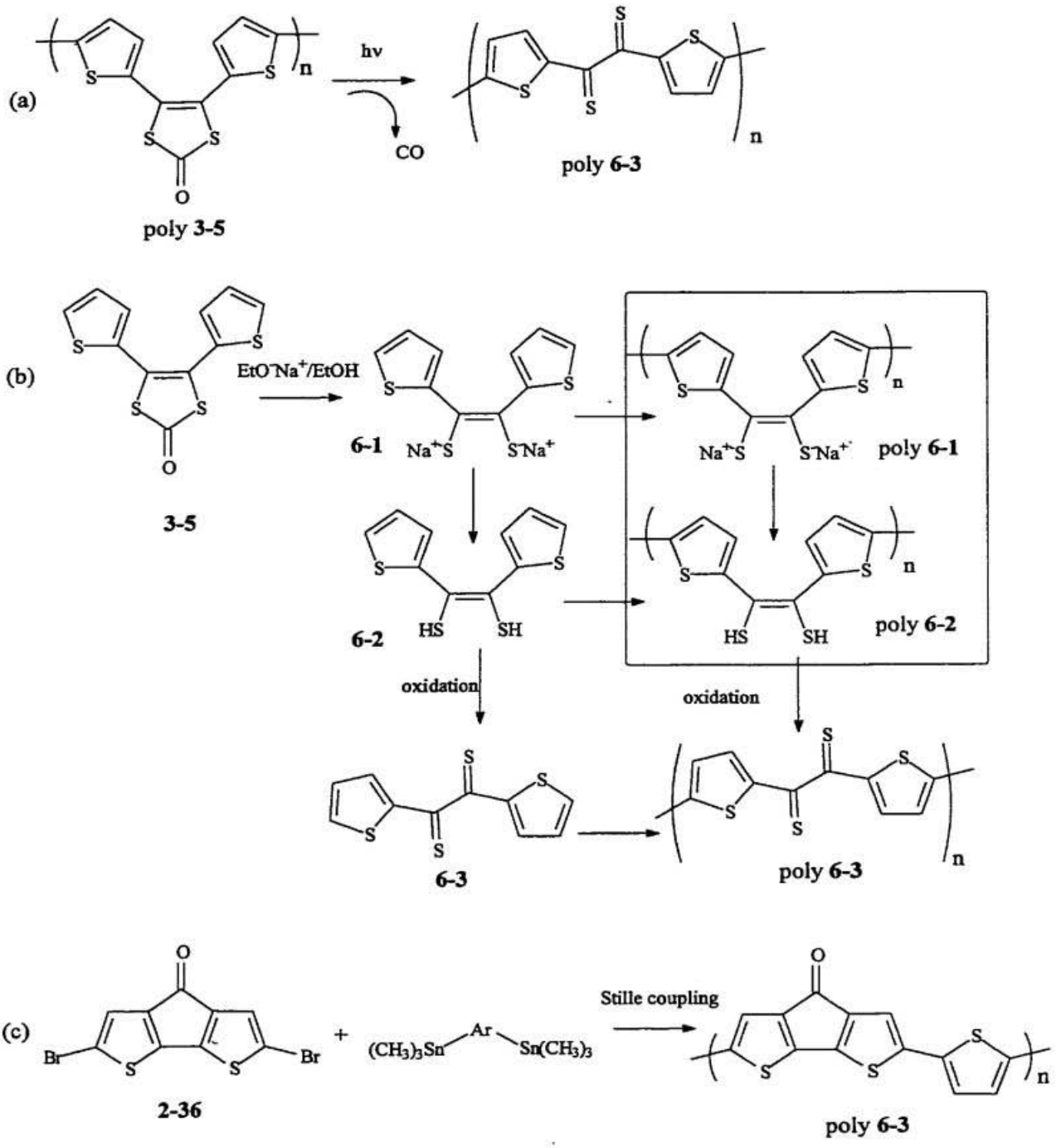


Figure 6-1. Plans of Future Work

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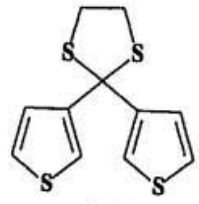
Appendix I

^{1}H NMR Spectra

Introduction

This appendix includes the ^{1}H NMR spectra for the *compounds presented* in this thesis. For the experimental details refer to section 2.4.1.



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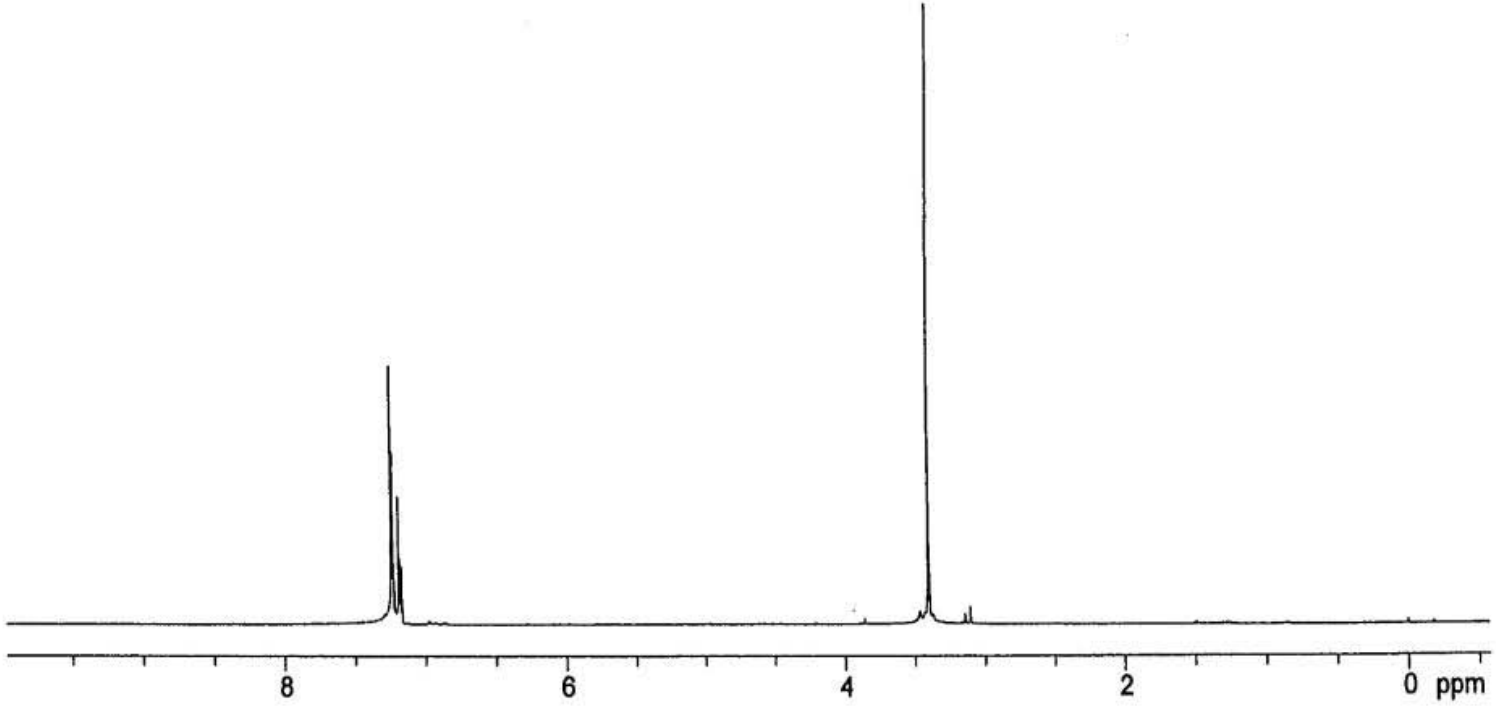

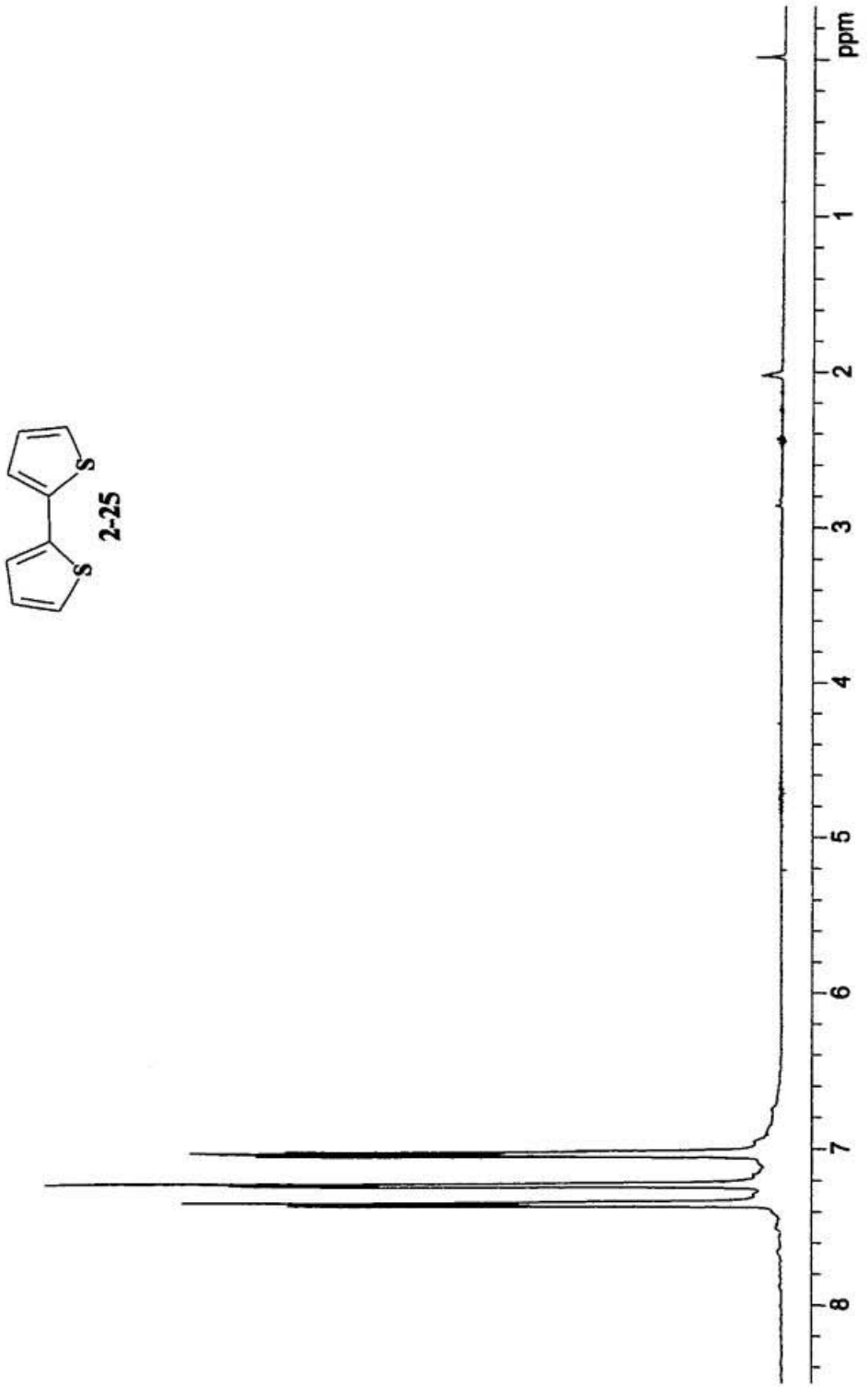
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2-25
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3
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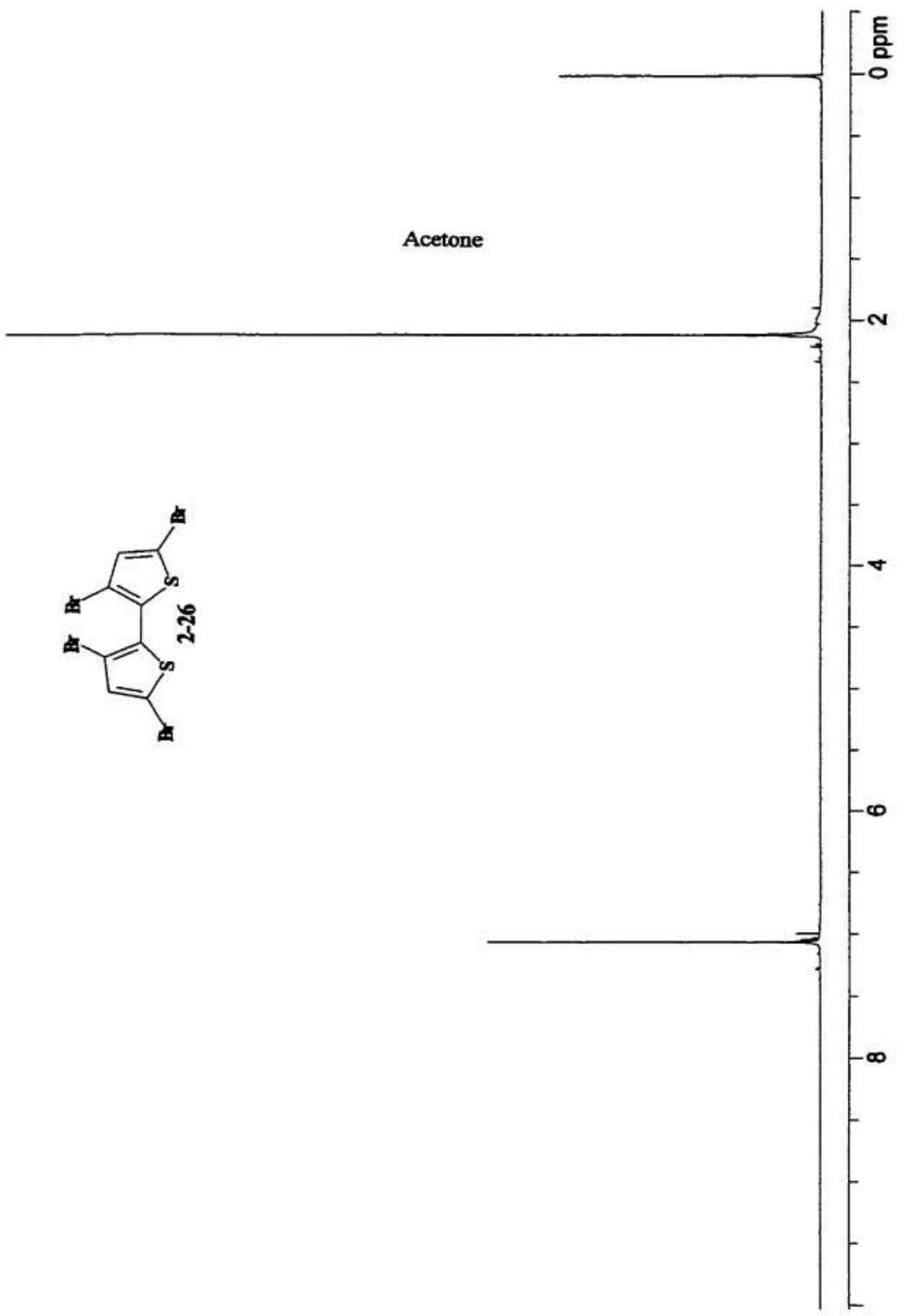
ppm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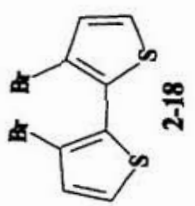
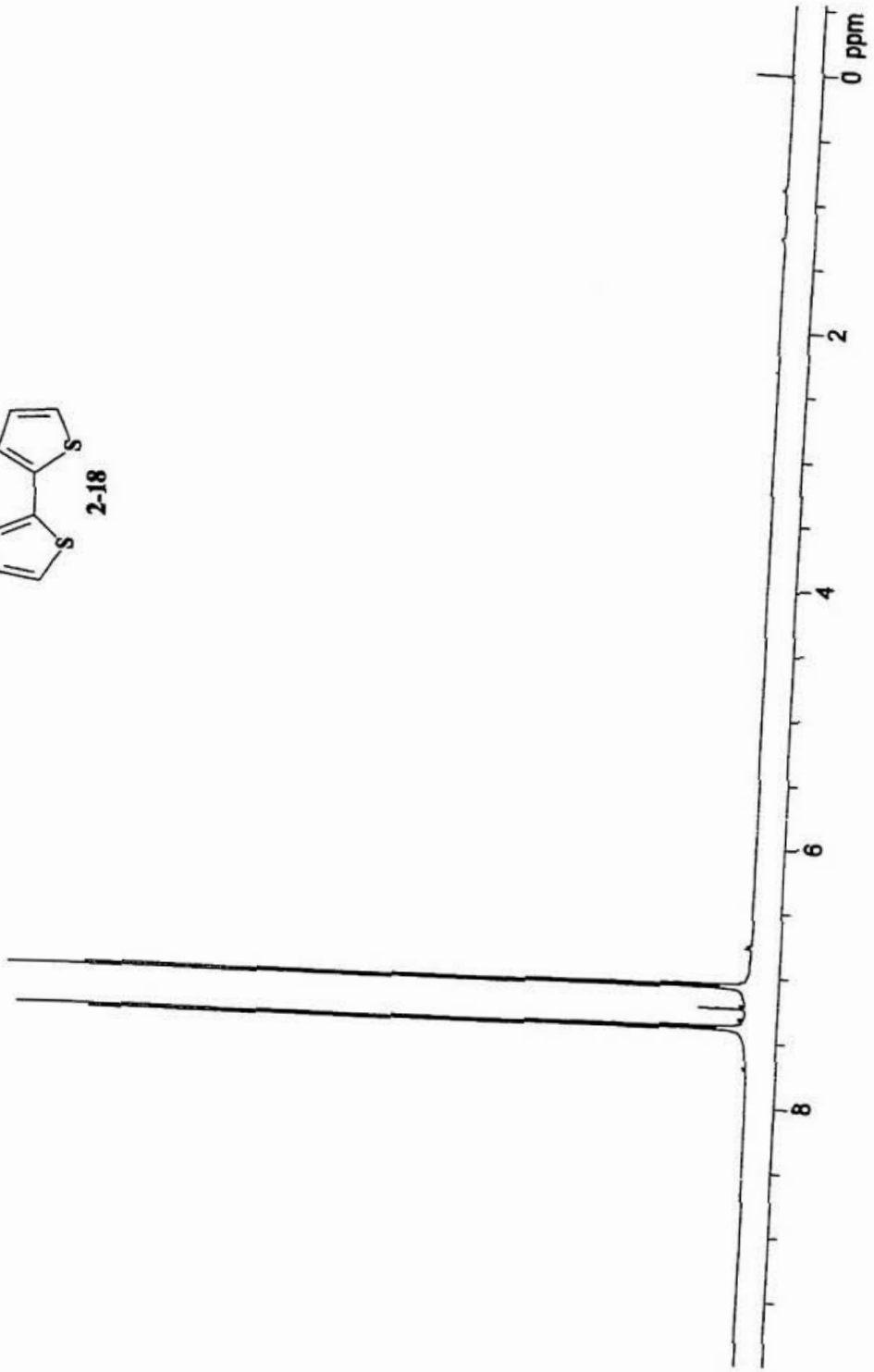
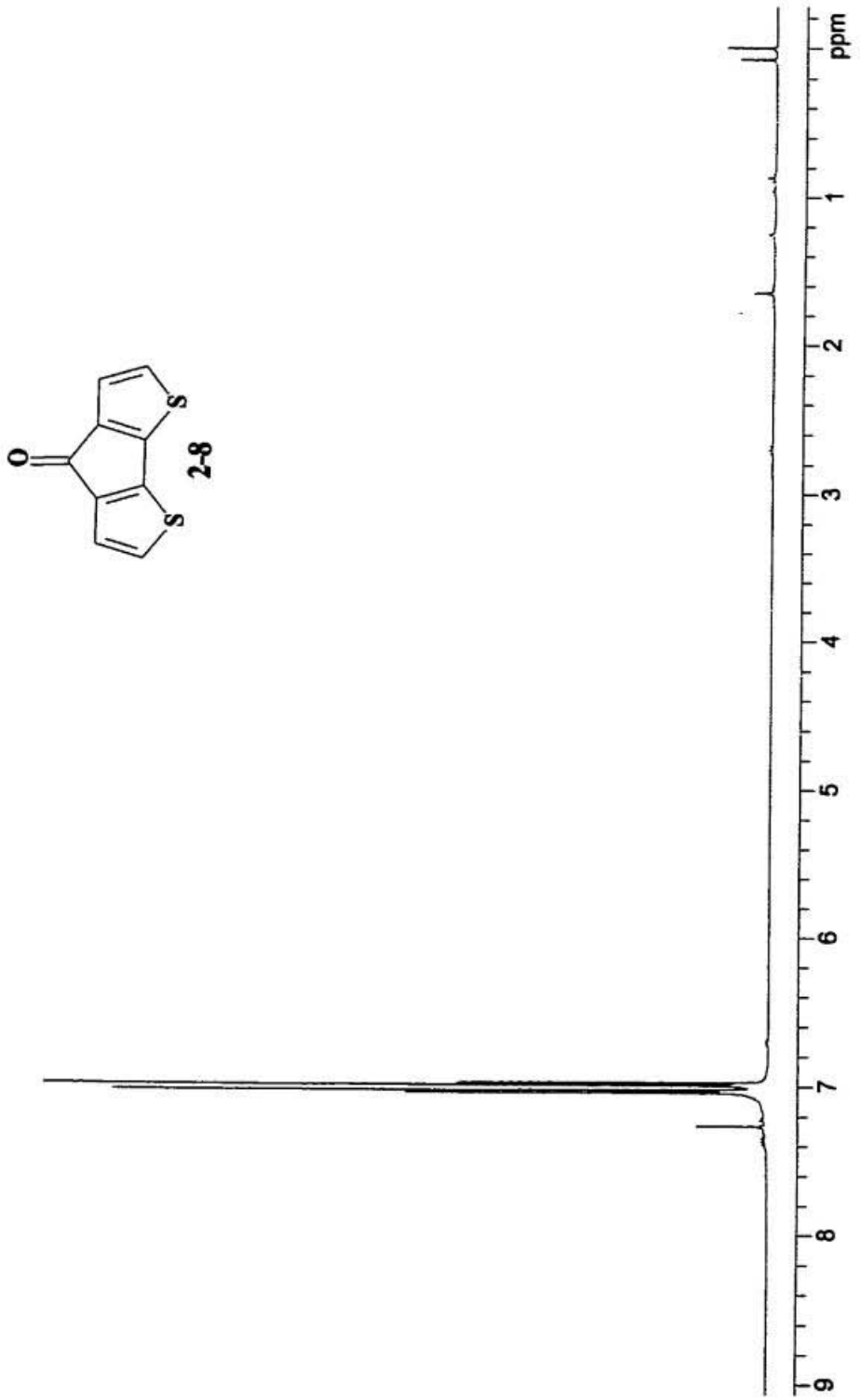
Br
Br
S
S
2-26



2-18

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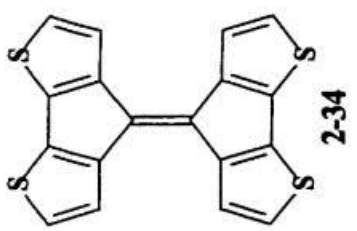
9



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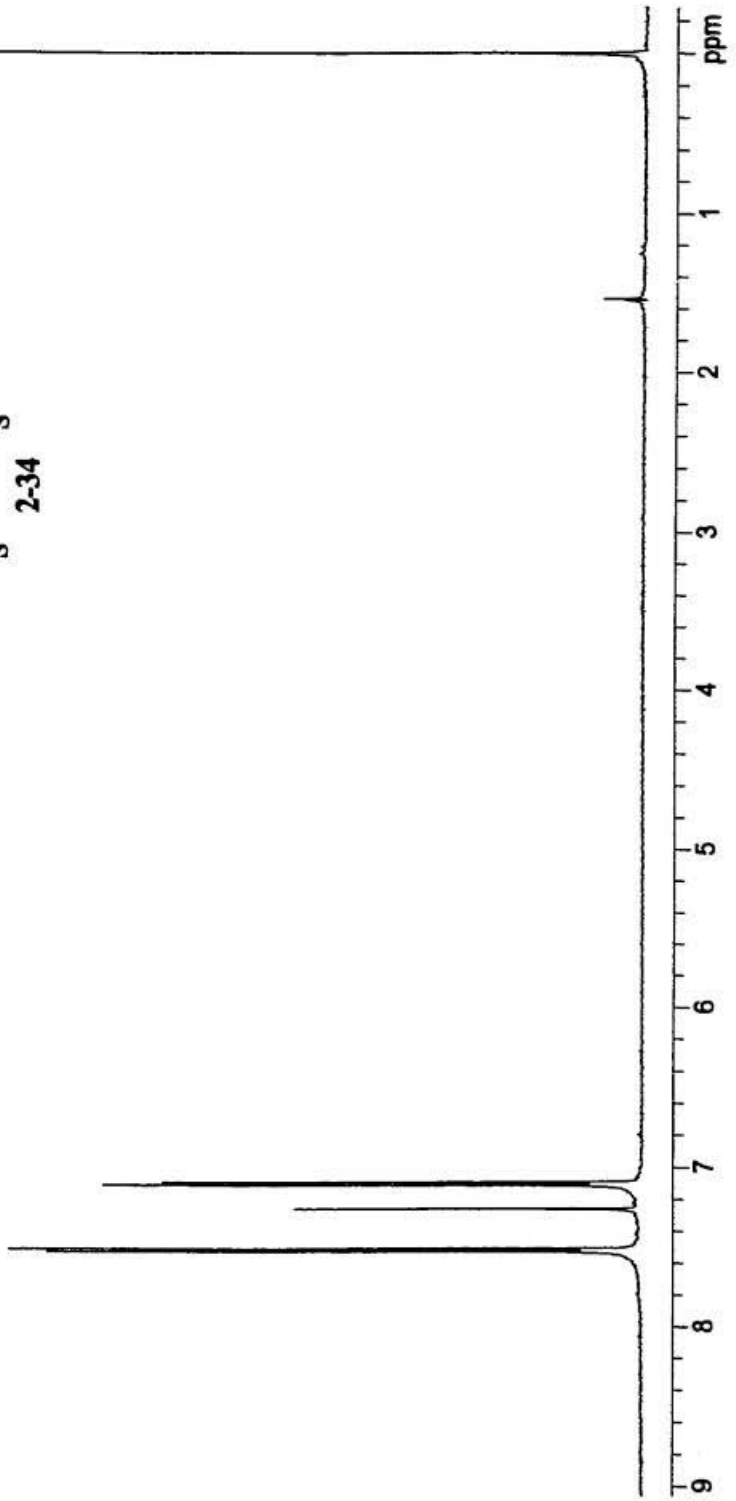
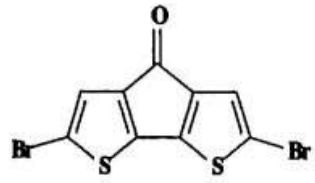
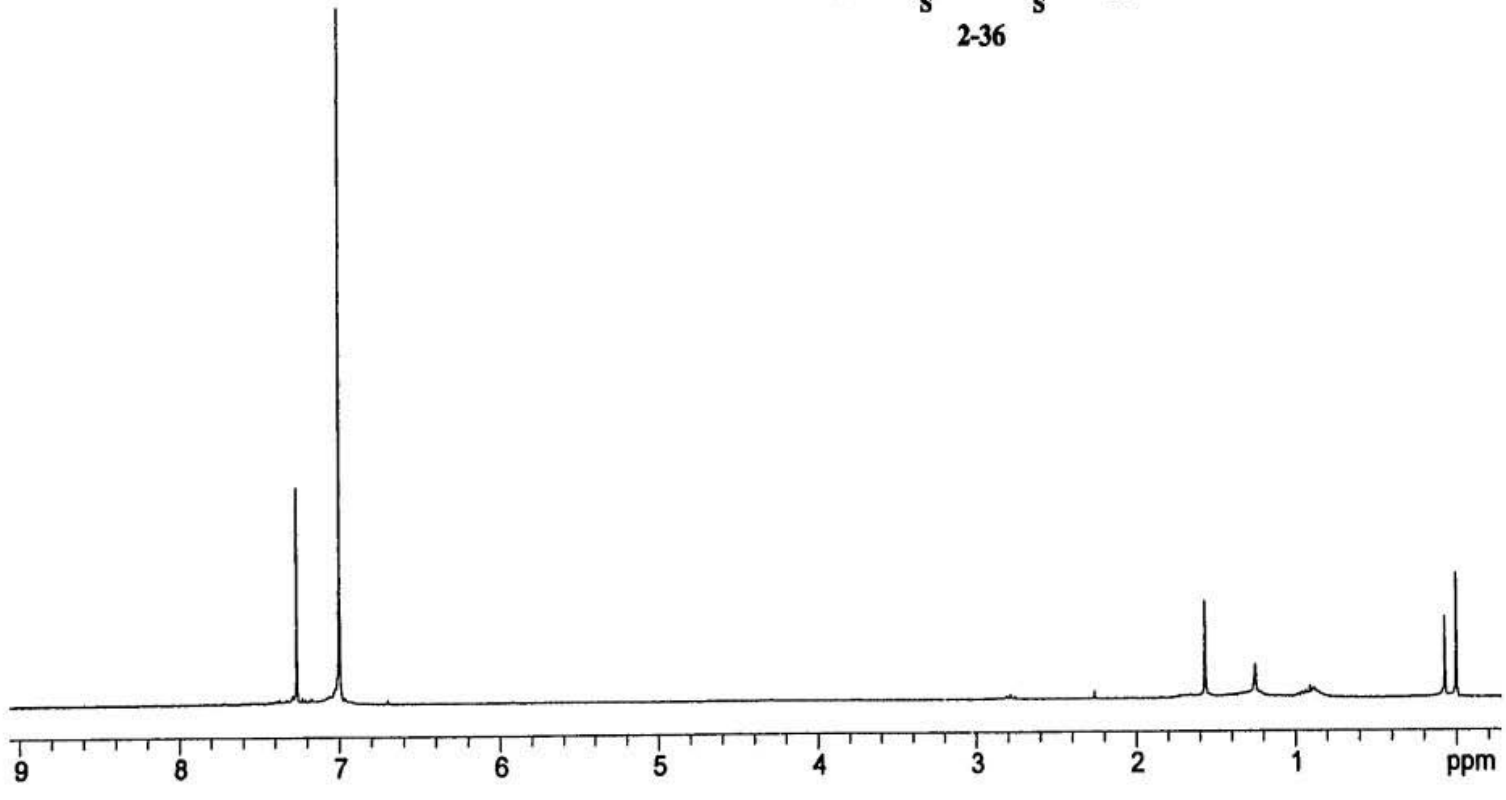
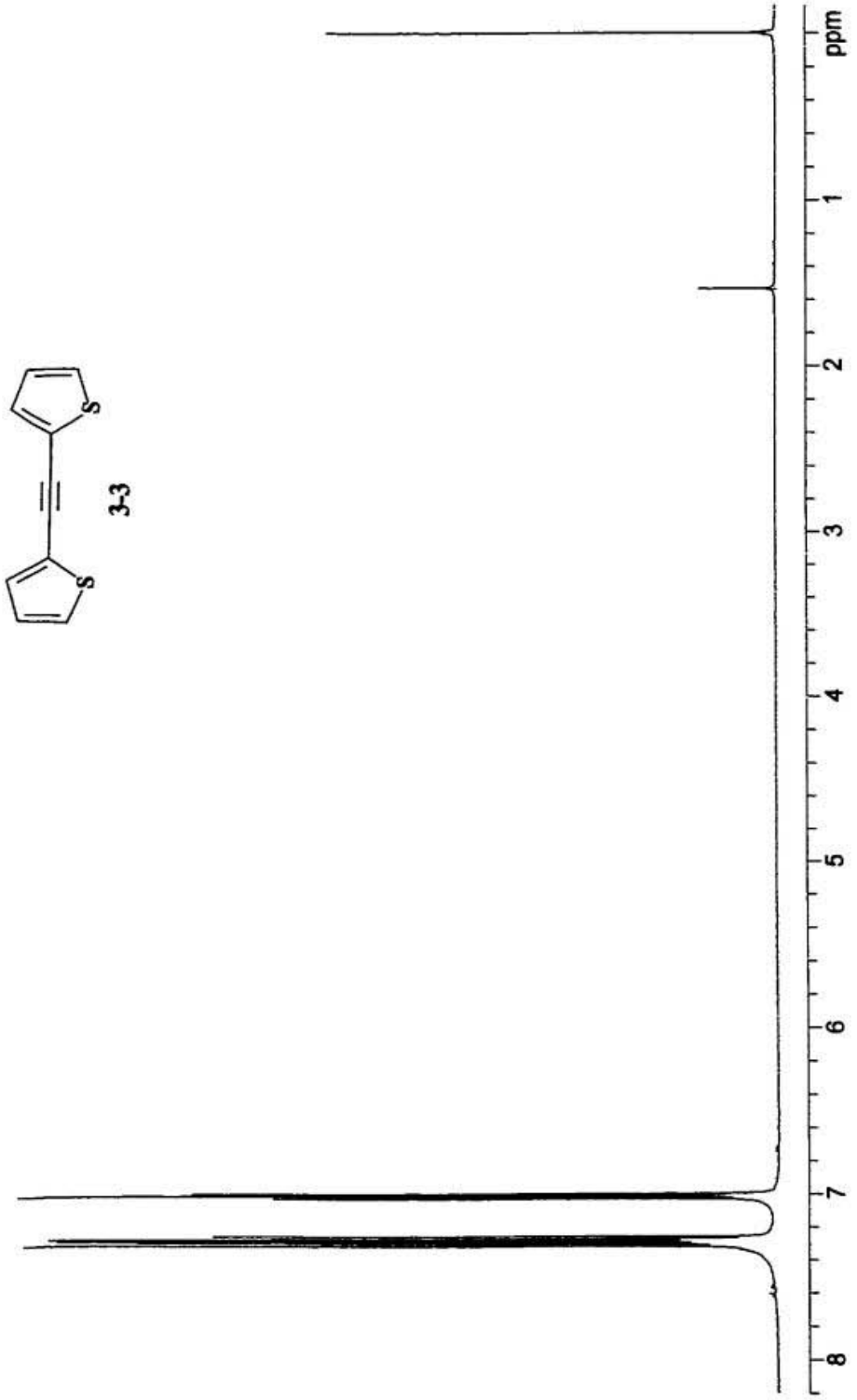




2-36

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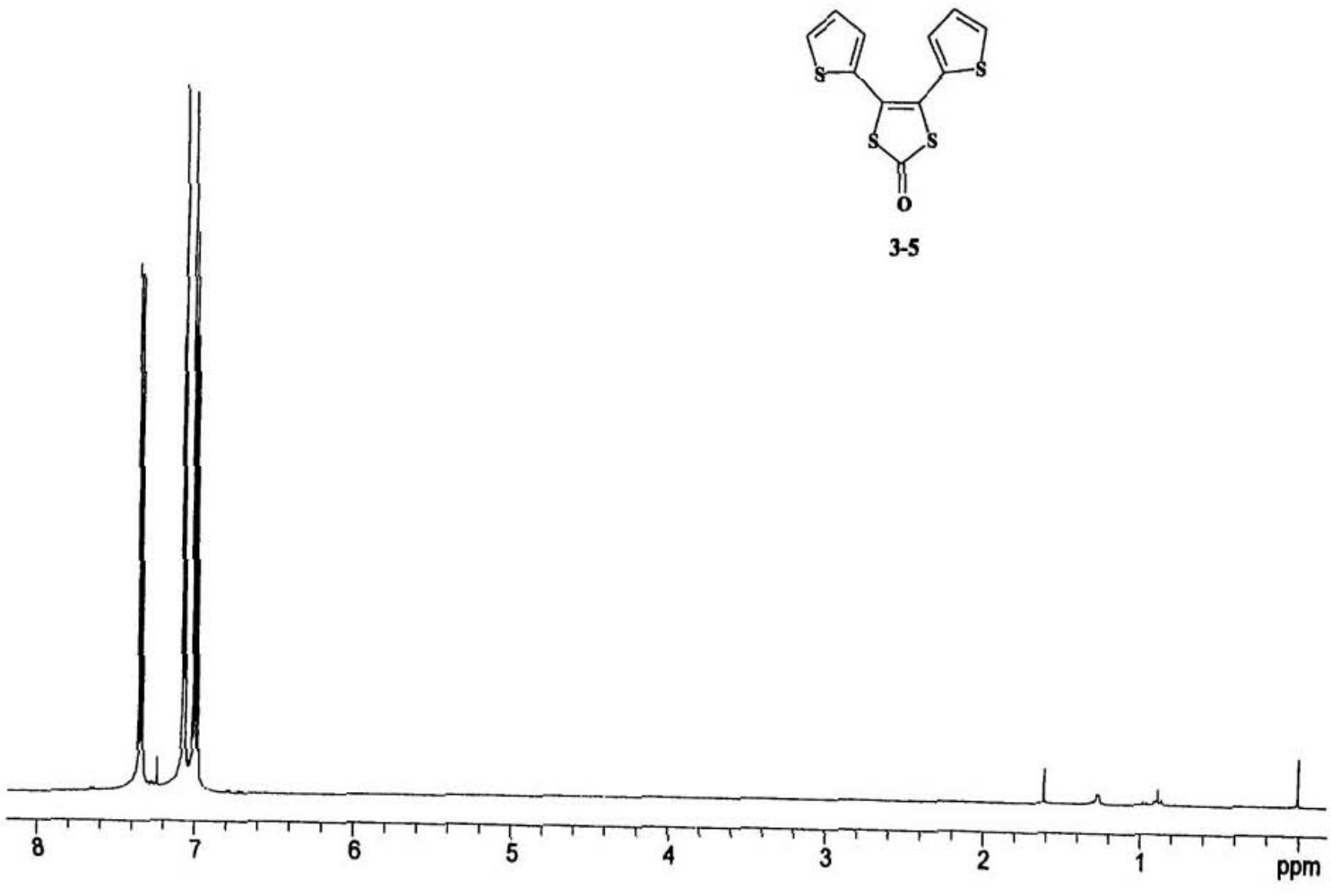
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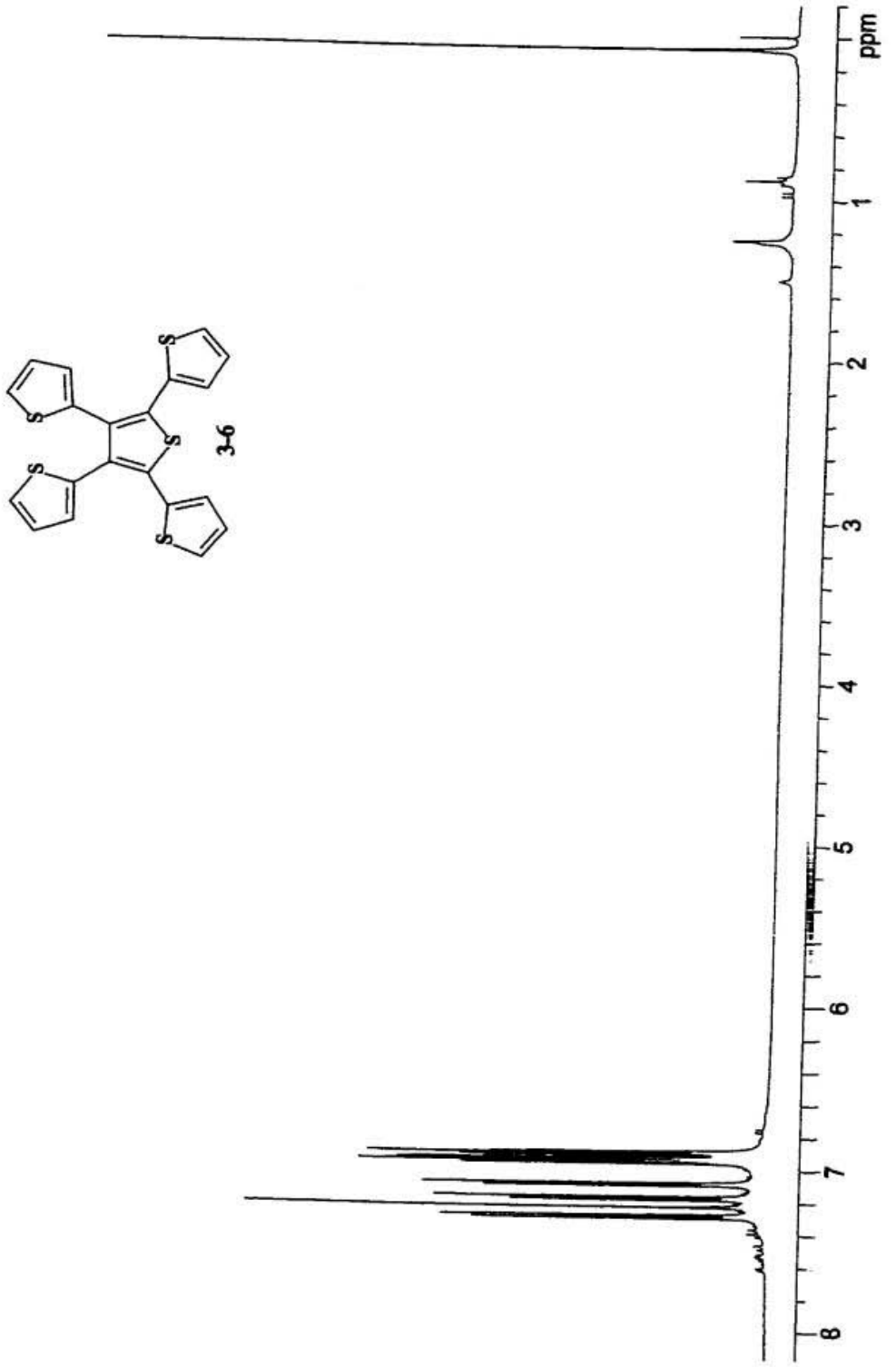
ppm


3-6
ppm
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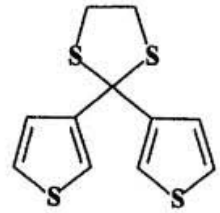
Appendix II

^{13}C NMR Spectra

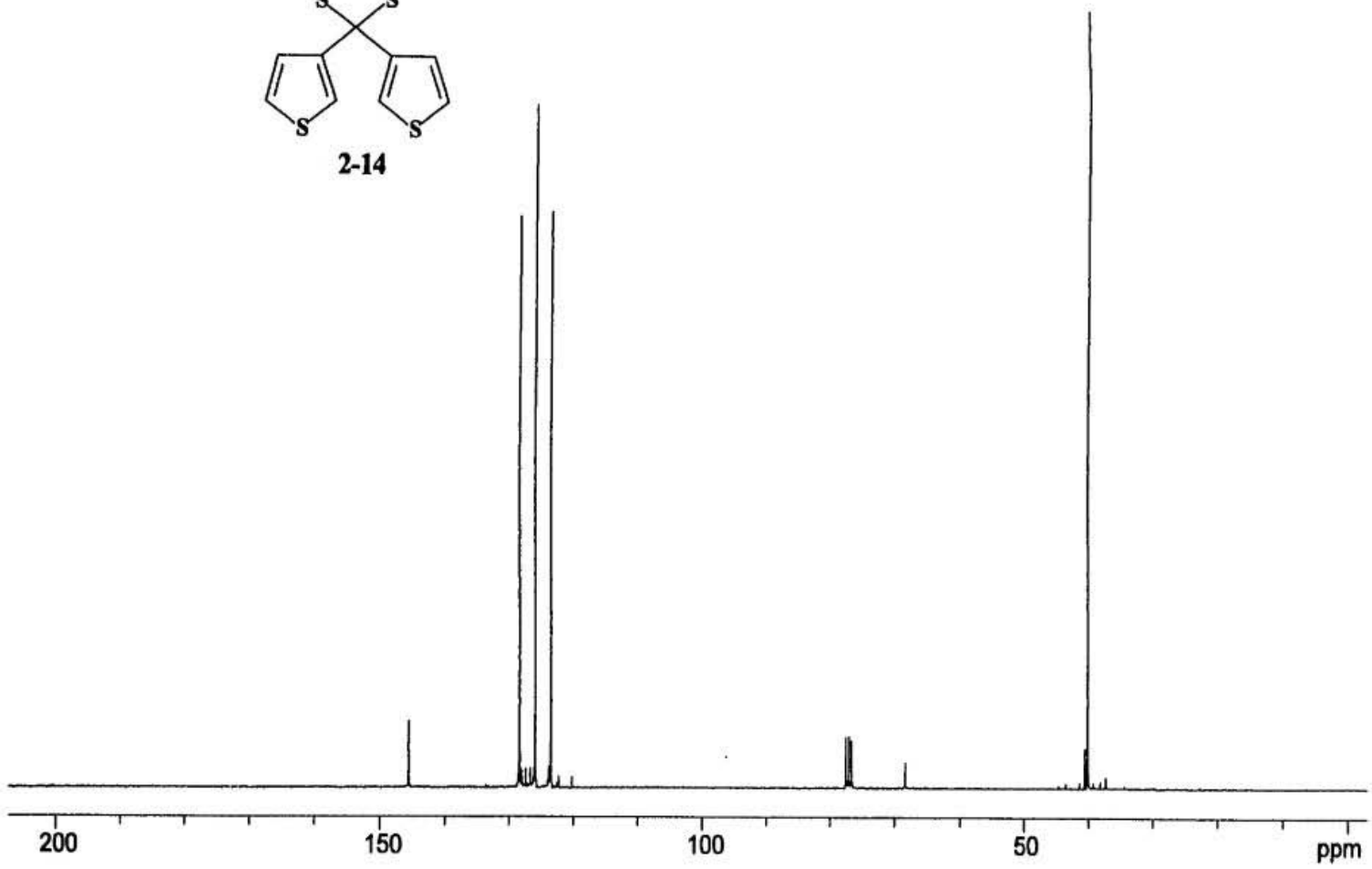
Introduction

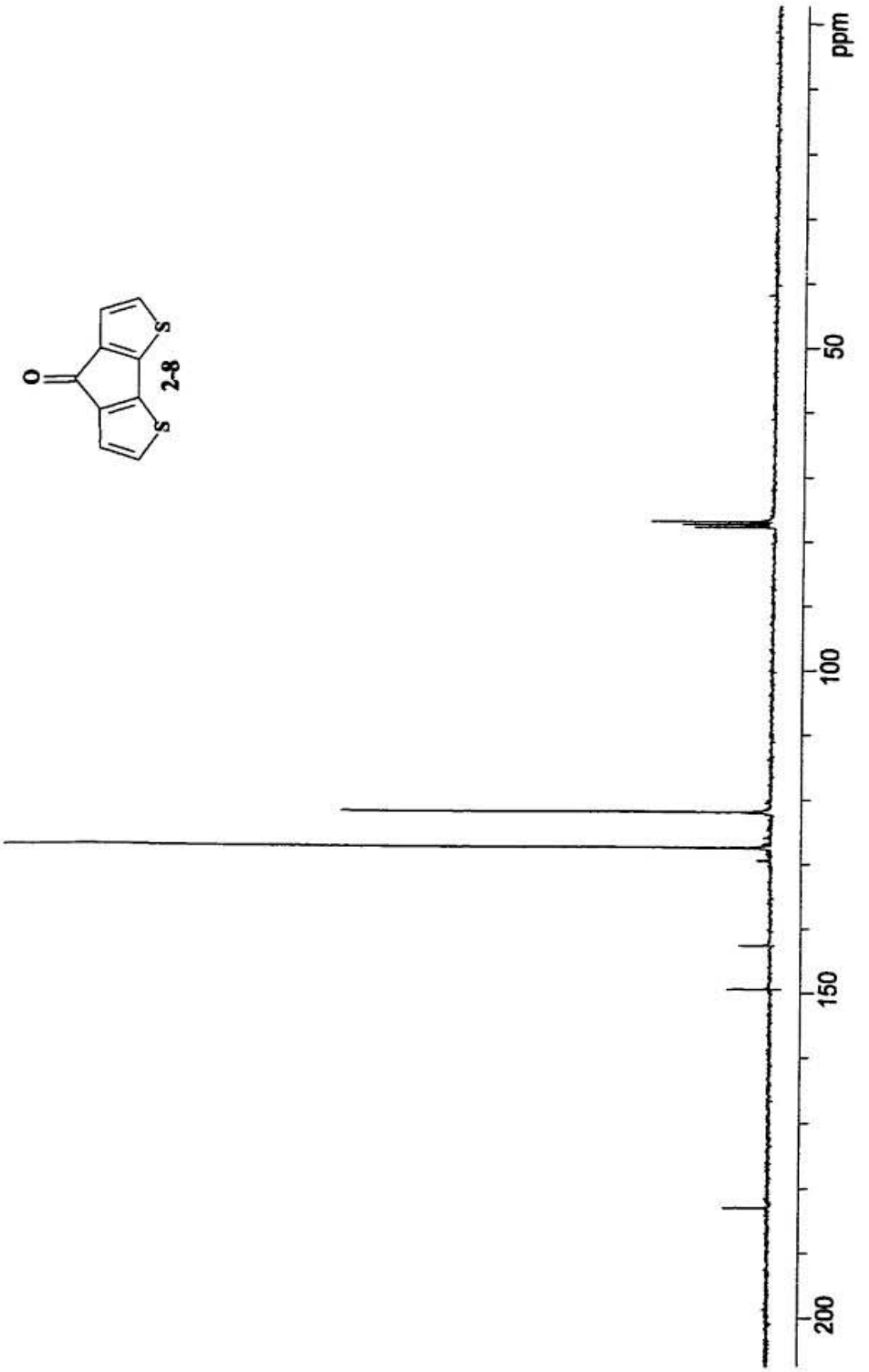
This appendix includes the ^{13}C NMR spectra for the compounds presented in this thesis. For the experimental details refer to section 2.4.1.

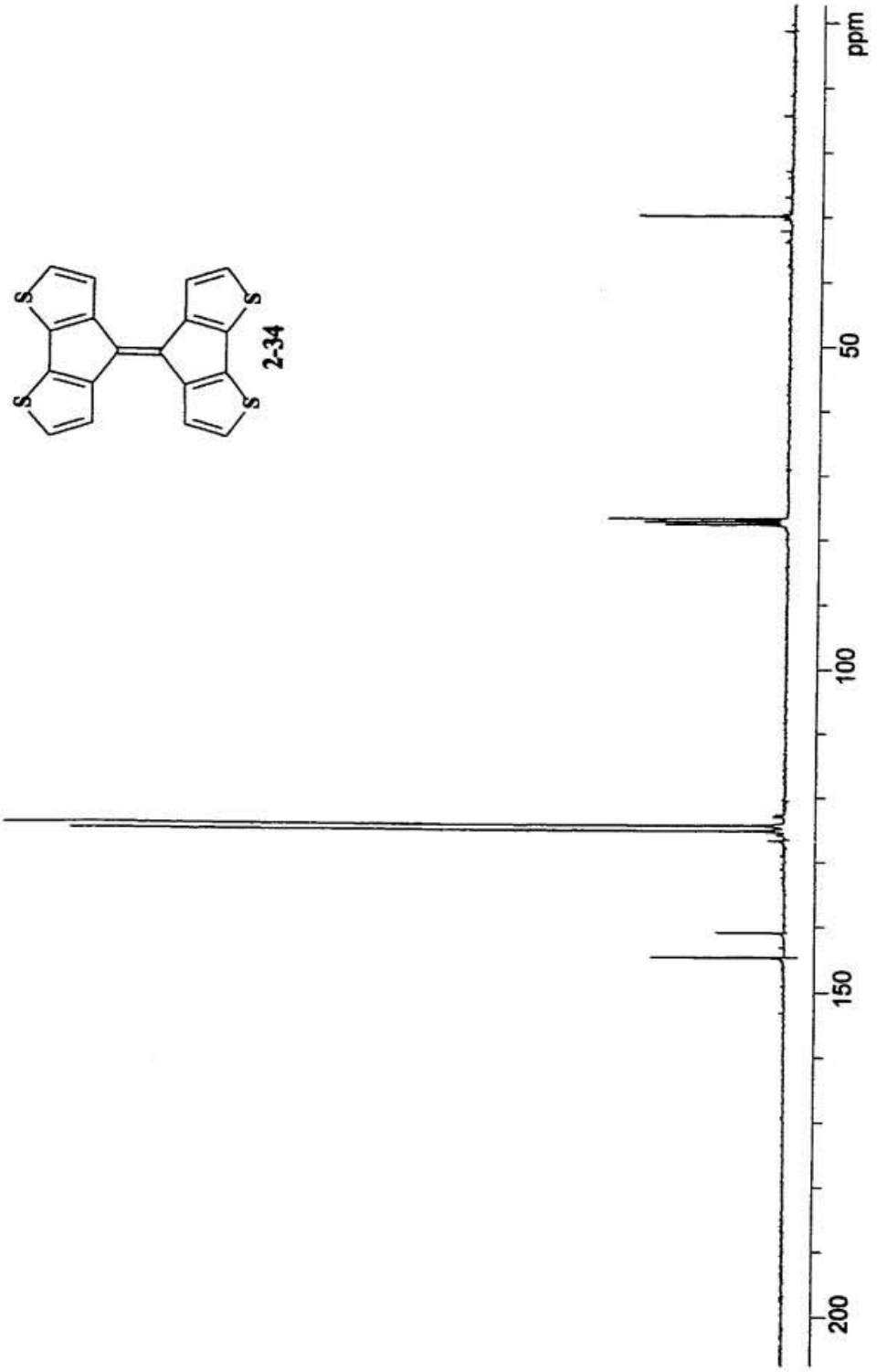
The spectra for compound **2-36** include a ^{13}C NMR spectrum and a ^{13}C NMR gated decoupling spectrum, which allowed us to distinguish **2-36** from its isomer 3,5-Dibromo-4*H*-cyclopenta[2,1-*b*;3',4'-*b*']dithiophen-4-one. The carbon signals at 139.7 ppm and at 114.2 ppm were both split into doublets by decoupling, indicating that both carbons are in α-positions relative to the carbon bonded to hydrogen. This occurs in **2-36** but not in the 3,5-dibromo isomer. The signal at *ca.* 120 ppm is a known artifact.



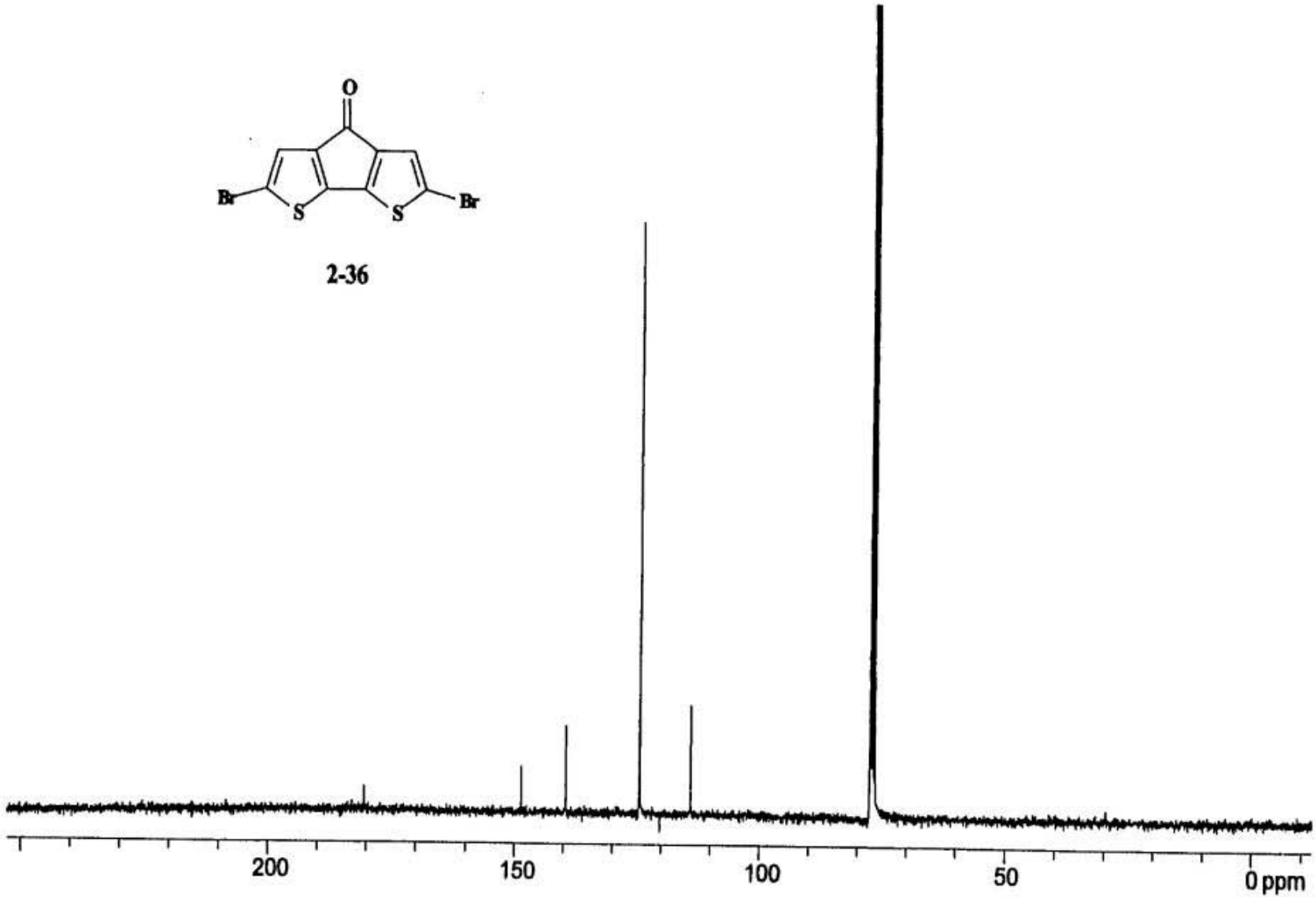
2-14

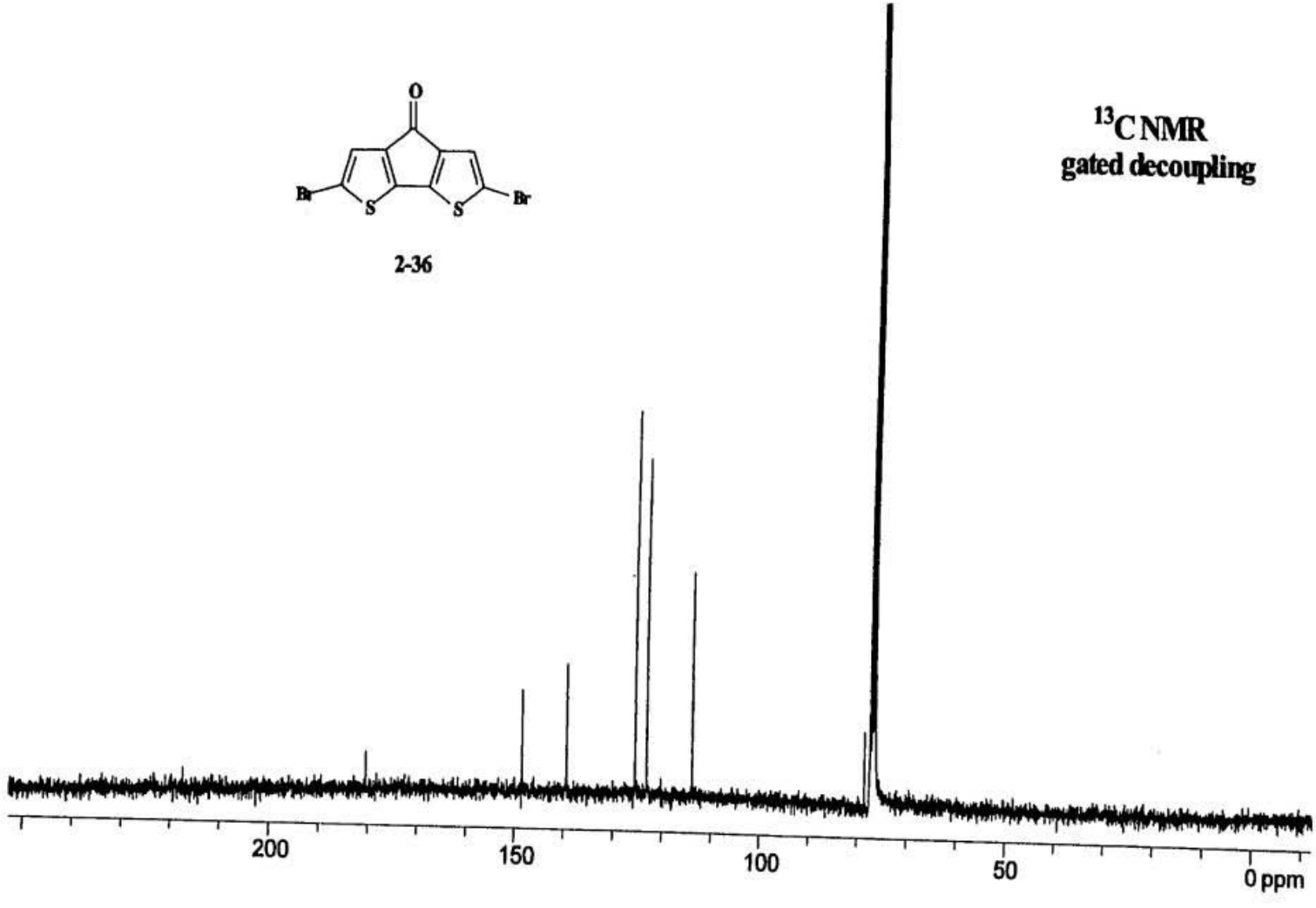



O
S
S
2-8
ppm
50
100
150
200

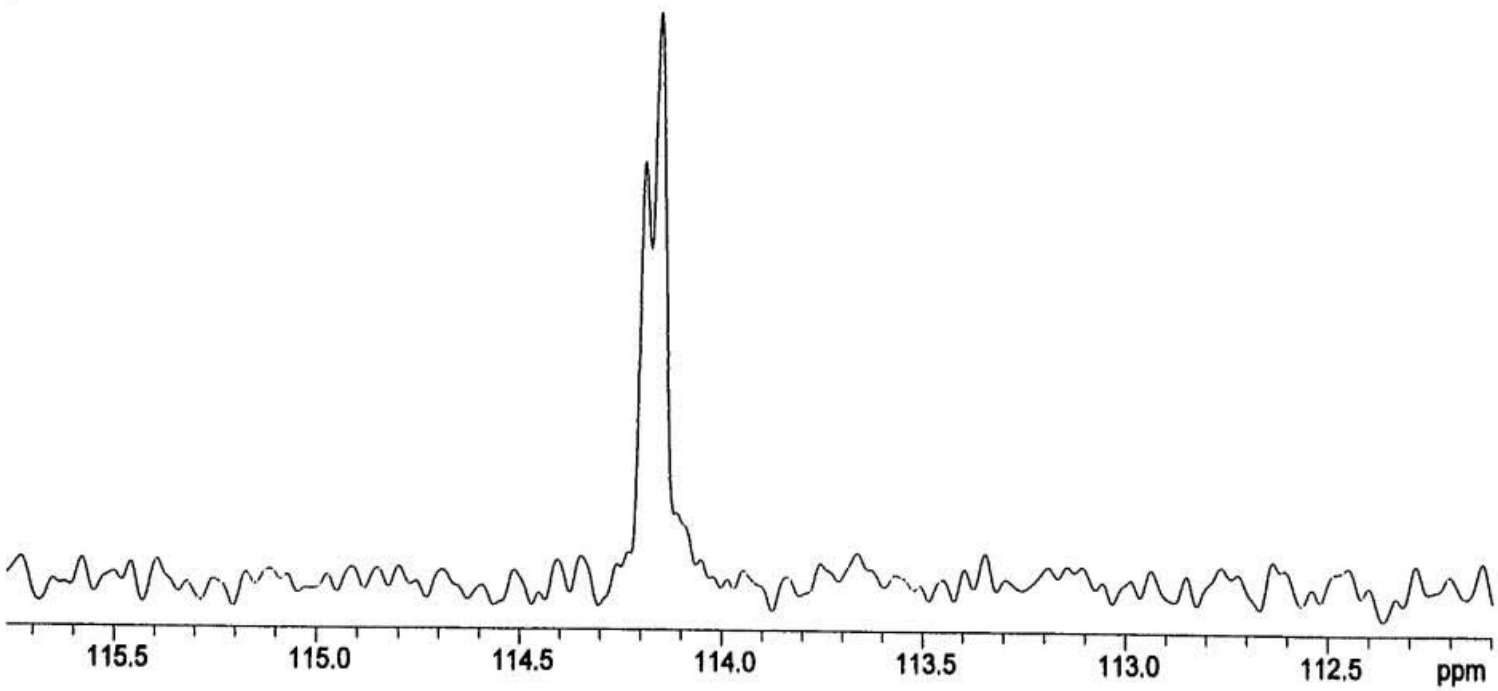

S
S
S
S
2-34
ppm
50
100
150
200

2-36

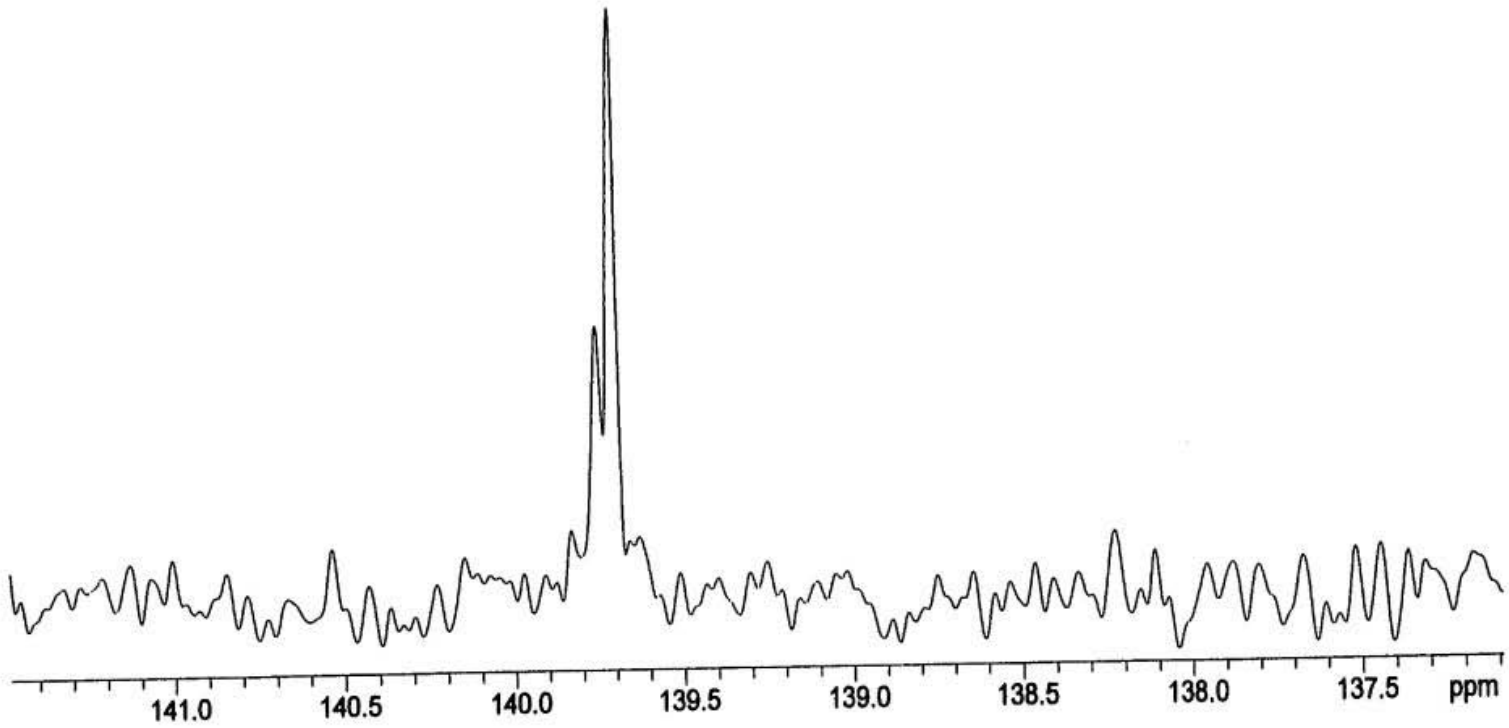


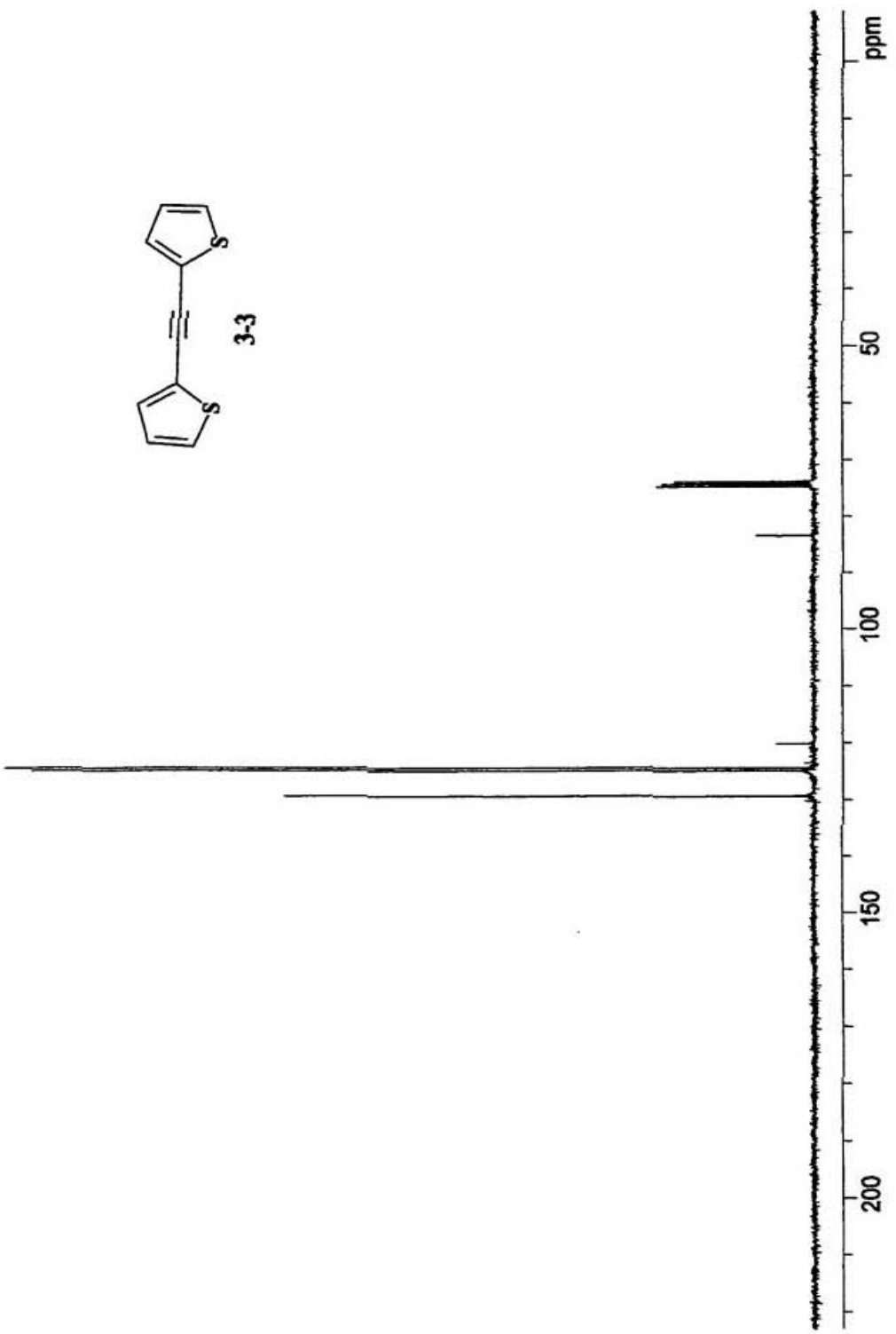

O
Br
S
S
Br
2-36
^{13}C NMR
gated decoupling
200
150
100
50
0 ppm

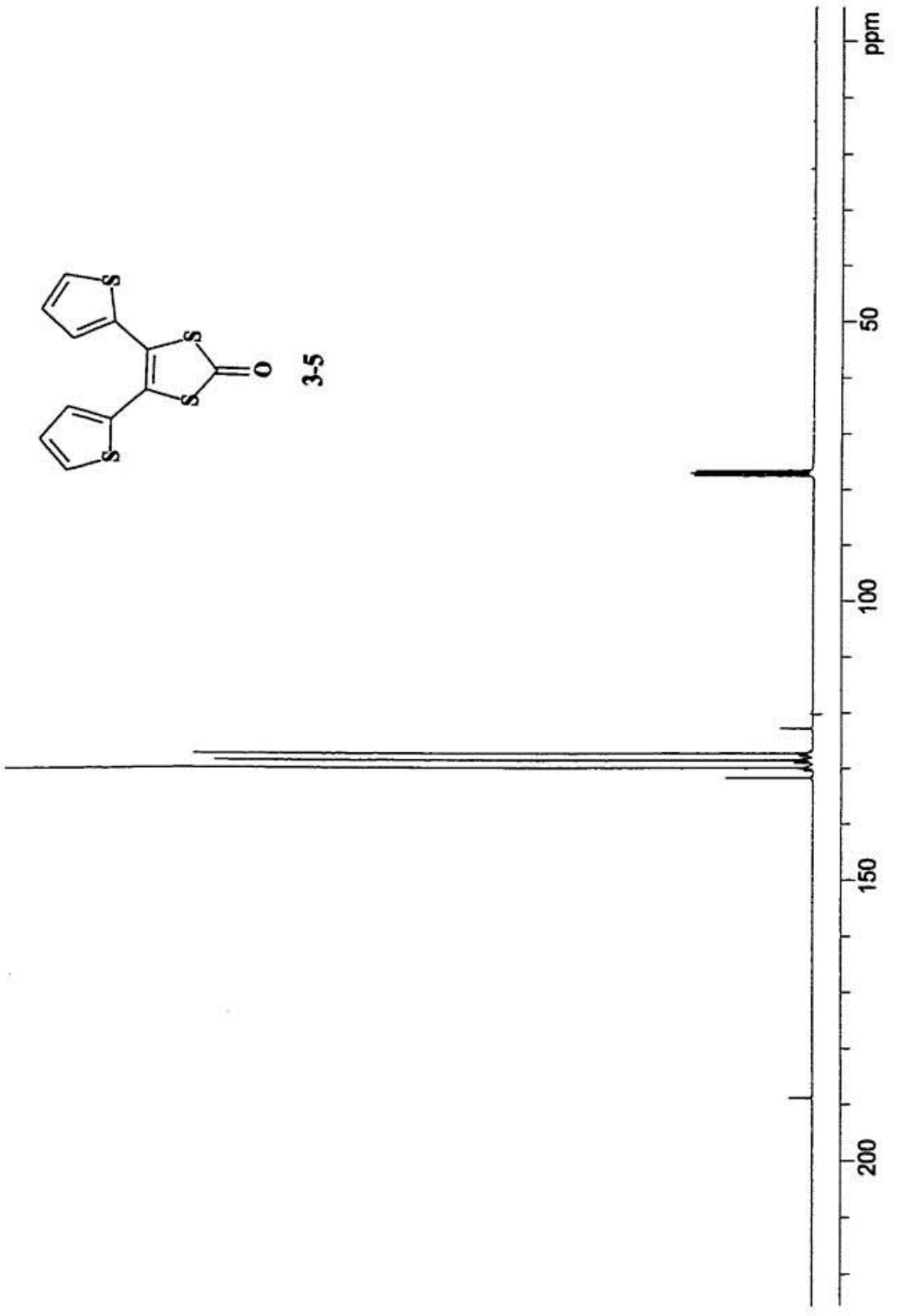
Enlargement of the signal at 114.2 ppm

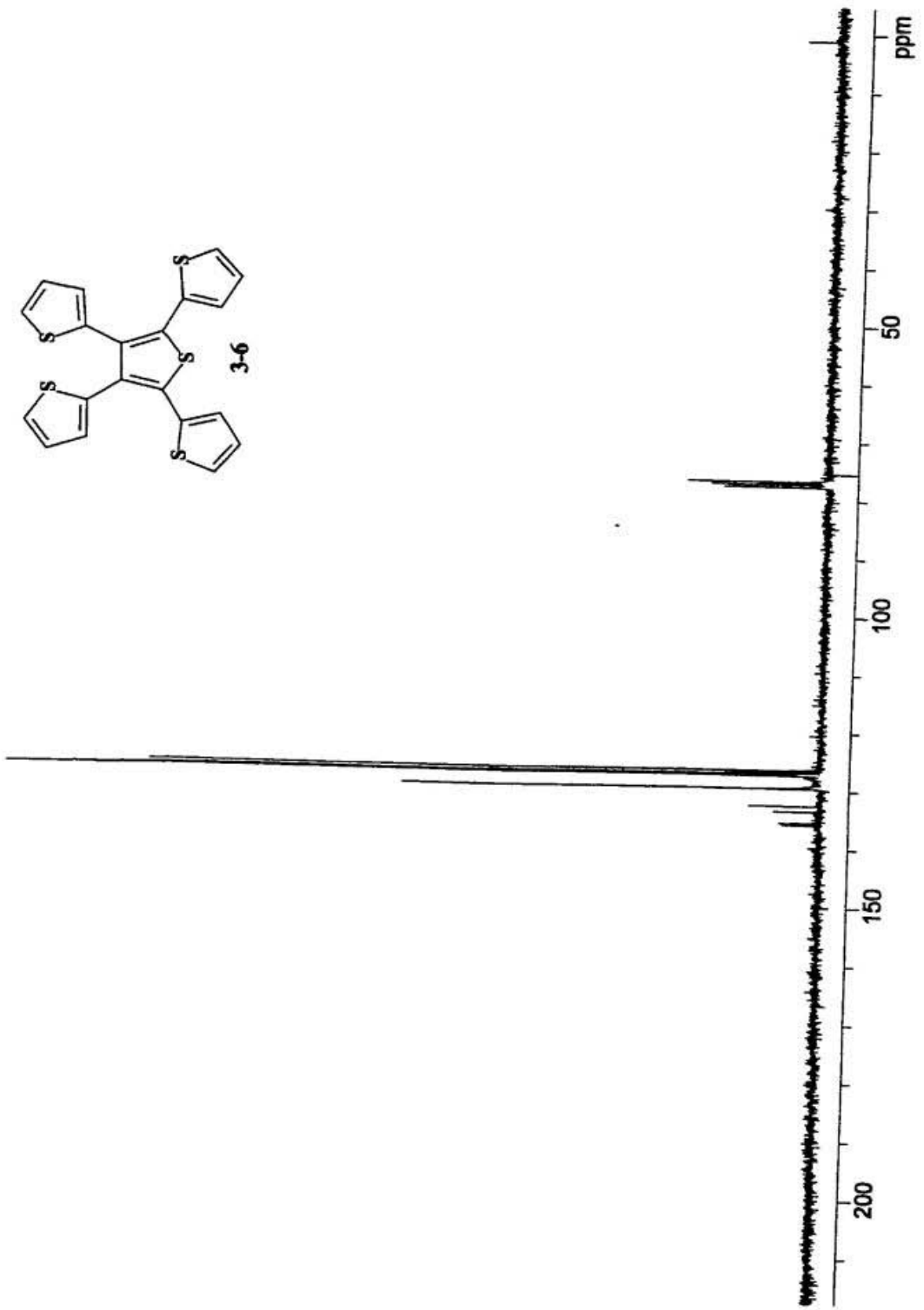


Enlargement of the signal at 139.7 ppm




S
S
3-3
ppm
50
100
150
200


S
S
S
O
S
3-5
ppm
50
100
150
200


3-6
ppm
50
100
150
200